SYNTHESIS OF ORGANOMETALLIC COMPOUND OF CHALOGEN

बुन्देलखण्ड विश्वविद्यालय, झाँसी

**A THESIS
SUBMITTED TO
BUNDELKHAND UNIVERSITY
FOR THE
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DOCTOR OF PHILOSOPHY
IN
CHEMISTRY
BY**
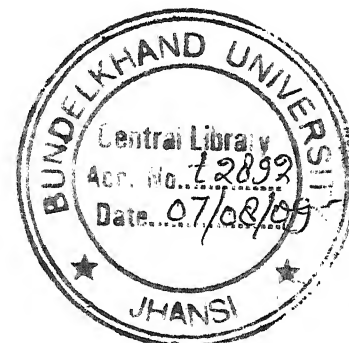
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INDIA

JUNE 2005

Dedicated

To My

Parents, Wife,

Brother

&

Sister

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Date : 1.0.06.05

CERTIFICATE

Certified that the work embodied in this thesis entitled **Synthesis of Organometallic Compounds of Chalogen** is the result of original researches carried out by **Mr. Anil Kumar,** Lecturer in Chemistry B.B.C. (P.G.) College, Jhansi under my supervision and is suitable for submission for the award of Ph.D. Degree of University of Bundelkhand, Jhansi.

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S. Srivastava

Prof. Shekhar Srivastava

DECLARATION

I here by declare that the thesis intitlled **Synthesis of Organometallic Compounds of Chalogen** being submitted for the degree of **Doctor of Philosophy** to the Bundelkhand University, Jhansi (U.P.), is an innovative piece of work carried out with utmost dedication by me, and to the best of my knowledge and belief it has not been submitted elsewhere.

Place :- Jhansi

Date : ...10.06.05...

Anil Kumar
(Lect. in Chemistry,
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ACKNOWLEDGEMENT

CONTENTS

CHAPTER - I

INTRODUCTION

Organometallic chemistry is a study of the compounds containing at least one direct metal-carbom bond. The term 'metal' is, however, difficult to define with precision. Elements having electronegativity less than that of carbon can be considered as metals, giving rise to 'a carbon metal bond with a differential higher electron density around the carbon atom. Thus, the organometallic compounds contain an anionic carbon.

The importance of organometallic compounds is manifold . The field of synthetic organic chemistry is well established. Further, the electron deficient bridging structure of metal alkyls, the sandwich configuration of ferrocene type compounds[1] and the unusual metal valence state of certain organometallic compounds[2] have necessiated a drastic revision in the old concepts of structure and bonding and have played a prominent role in advancing new theories of valency. The biological activity of many organometallic compounds have been a new asset to the mankind.

The organometallic chemistry of many main group elements are well known and exhaustively covered in several reviews and books[3-14]. In contrast to this, the organometallic chemistry of group VI A elements, in general, and tellurium in particular, has been little studied.

The first organic derivative of tellurium, dialkyltelluride, was prepared by wholeler in 1840[15]. At first, the organotellurium chemistry remained unexplored but later on, it was pursued mostly as an extension to corresponding selenium

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chemistry. But now it is quite clear that there are at least as many dissimilarities as there are similarities in the chemical behaviour of selenium and tellurium. Some of the workers who greatly enriched the knowledge of organotellurium chemistry include Lederer (1910-1920); Morgan, Drew and co-workers (1920-1935); Petragnani demoura campos and co-workers (1960-70) and Schumann and co-workers (since 1963). Some recent creditable work by Irgolic have appeared in the form of several reviews and books[16-18].

Organotellurium compounds are highly toxic and the effect is often cumulative[19-22]. Large doses paralyses nerve structure and cause headache, nausea and eczema[23-24]. Continued inhalation of dimethyl telluride and other volatile tellurium compounds induces and unpleasant halitosis and debility and causes headache[25].

A paper describing the inhibitory action of cyclic tellurium compounds on the growth of bacteria appeared in 1922[26]. Taniyama and co-workers found that diaryltellurium dihalides possess a strong antibacterial action[27]. Oefele published a review on therapeutic agents containing tellurium[20]. Patents covering organic tellurium compounds have also been reported[28].

Tellurium is present in the earth's crust to the extent of 2×10^{-7} Percent by weight. However, it is generally obtained as a by-product of mining and processing operations of other ores. Today tellurium accumulates as a by-product of the electrolytic copper refining process. The anode sludge can contain

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up to 8% tellurium in addition to Se, Cu, Ag, Au, and Platinum group metals. Density of crystalline metals at 449.8⁰C to a dark liquid and boils at 1390⁰C[29]. A detailed discussion of the physical properties of tellurium is available in the literature[28].

The properties of the elements in subgroup VIA of the periodic table O, S, Se, Te, and Po undergo striking transition as the group is descended. The chemical behaviour of the group passes from that of the typical non metals O and S to the typical metal Po. A systematic change is also observed in the structure of the elements from diatomic molecules, through ring and chain molecules to a simple lattice compound of polonium atom. A corresponding transition in electrical properties accompanied the structure evolution. Thus, oxygen and sulphur are insulators, Se and Te are semiconductors and Po show metallic conduction.

The industrial applications of tellurium and its compounds have beeen described by champness[29], Nachtman[31], Aborn[31] and Cooper[32],. Their applications as rubber vulcanization, accelerators, antiknock agents, antioxidants, insecticides, lubricating oil additives, gel forming clays, curing agents for ethylene propylene terpolyments, Photoconductors,therapeutic agents, dye intermediates and wetting agents are well known[16].

The ecological aspects of tellurium in human and animals health, the toxicity and metabolism of tellurium compounds and the interaction of sodium tellurate with Hg, Cd, Se, Be and As have been reviewed[17].

Electronic Configuration and Stereochemistry

The elements of group VIA have a general electronic configuration [X] $ns^2 np_x^2 np_y^1 np_z^1$ (where x = inert gas core and 'n = 2 to 6 from oxygen to polonium) and tend to attain an inert gas configuration by gaining or sharing two electons. E^{2-} Ion, however, exists in case of oxygen only. The More electropositive elements S, Se and Te form only a few compounds which are more than 50% ionic. The formal oxidation states of II, IV are known for tellurium and are summarized in table I along with the possible stereochemistry.

Table : 1

Valency	CO. NO.	No. of bonds	No. of lone pairs	Geometry	Hybrisidisation	Examples
II	2	2	2	Angular	sp^3	$R_2Te,$, RTeX
	3	3	2	Pyramidal	sp^2d	$[RTeX_2]$
	4	4	2	Square-Planner	sp^3d^2	$Te[SC(NH_2)_2]Cl_2$, $PhTeX_2[SC(NH_2)_2]$
IV	4	4	1	Trigonal Bipyramidal Tetrahedral	sp^3d	R_2TeX_2, RTeX$_3$ R_4Te $R_3Te^+X^-$
	5	5	1	Square-pyramidal	sp^3d^2	$[RTeX_4]^-$, RTeX3.L (L=Monodentate)

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	6	6	1	Octahedral	sp^3d^3	$[R_2TeX_4]^{2-}$,$RTeX_3L$ (L=Bidentate)
	7	7	1	Distorted pentagonal bipyramidal	sp^3d^4	$RTe_2[Et_2NCS_2]_3$
	8	8	1	Distorted dodecahedral	sp^3d^5	$Te(Et_2NCS_2)_4$
VI	6	6	no	Octahedral	sp^3d^2	$C_2F_5TeF_4Cl$, $(C_2F_5)_2TeF_4$
	8	8	no	-	$sp3d^4$	TeF_8^{2-} $TeF_6.2R_3N$

Fig. 1 : Possible oxidation states in tellurium

Te has in the ground state, two unpaired electrons and hence oxidation state(II) is well known. In such compounds one 's' and three 'p' orbitals hybridise, giving four sp³ hybrid orbitals, of which, two are occupied by lone

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pairs and the remaining two have bonding electron pairs. The geometry is thus 'V' shaped(Fig.2).
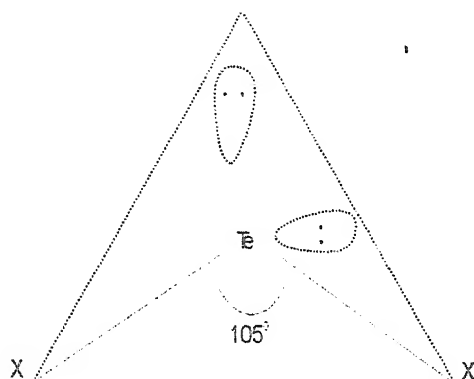
Fig. 2: V-shaped structure for Te(II) compounds

In the first excited state, compounds with tellurium in oxidation state (IV) are obtained by uncoupling the p_x^2 electrons: one of them being promoted to the empty d orbitals, resulting in the formation of five of sp^3d hybrid orbitals of equivalent energy, directed trigonal bipyramidally in spaces about the metal atom (Fig.3).
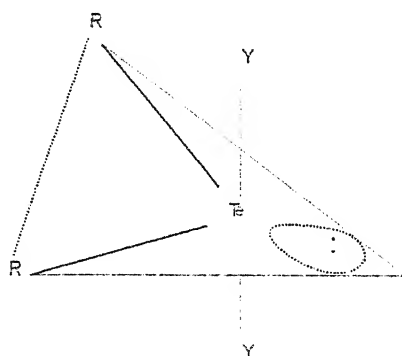
Fig.3: Trigonal bipyramidal structure for Te(IV) compounds

In the first excited state, coordination number greater than four is achieved by accepting electrons with suitable donors in the empty d-orbitals. The for-

mation of penta-and hexa-cooradinated molecules is visualises on the basis of sp^3d^3 and sp^3d^2 hybridisation with one lone pair of electrons resulting in pseudooctahedral and octahedral structures respectively[33-35]. (Fig.4 and 5).
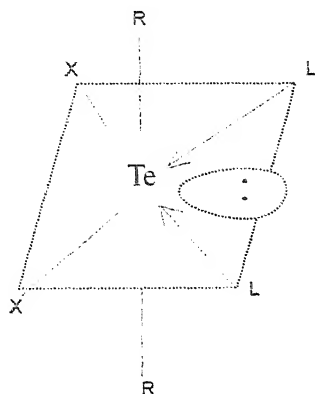
Fig.4: sp^3d^3 pseudooctahedral   Fig.5: sp^3d^2 Octahedral
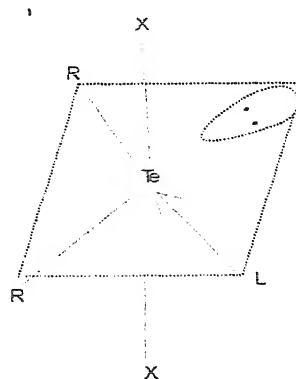
Coordination number greater than six are rare. A sp^3d^4 hybridised tellurium dithiocarbamate with stereochemically inert lone pair of electrons has been reported[36]. Hepta and octacoordinated tellurium atom having sp^3d^4 and sp^3d^5 hybridisation have also been reported by steinar et al[37-38]. (Fig.6).
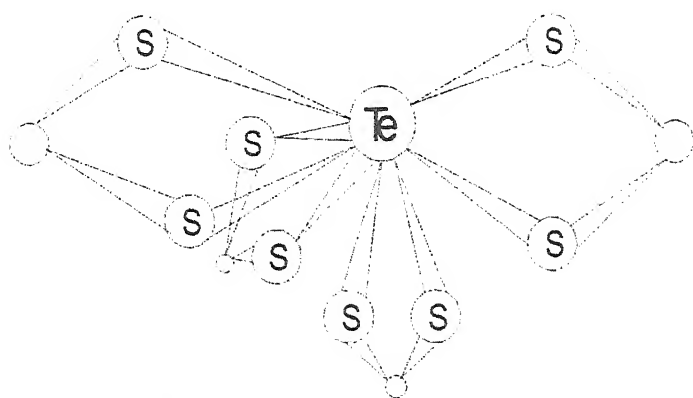
(All Et$_2$ N-groups are omitted and the samallest spheres represent carbon atom)

Fig.6: Te(Et$_2$NCS$_2$)$_4$

In the second excited state, all the six electrons of outer most orbit of tellurium get uncoupled resulting in sp^3d^2 orbital formation, which are directed

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octahedrally about the metal atom[39-40].

TeF$_6$, C$_2$F$_5$TeF$_4$Cl and (C$_2$F$_5$)$_2$TeF$_4$ having regular octahedral structure have been confirmed by IR (Fig.7)
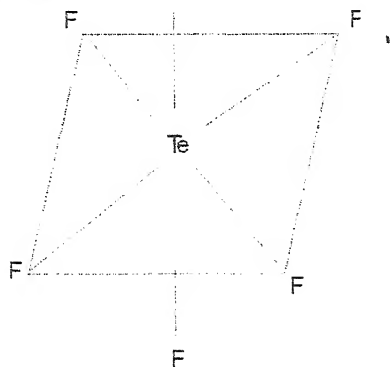
Fig.7: Regular octahedral structure of Te F$_6$

Low lying d-orbitals in the outermost valency shell of tellurium are thus involved in the expansion of covalency. The stable coordination compounds with electron donors may be formed when a pronounced stabilisation occurs through the participation of vacant d-orbital. The additional bonds in espansion of bi-and tetra covalency of tellurium may be of the following types:

Dσ – bonding : In which there is an overlap of s-orbital of the donor atom with d-orbital of the metal atom e.g., in R$_2$TeX$_2$.nNH$_3$.

dπ – bonding: Here the empty d-orbital of the metal overlap with the filled p or d orbitals of adjacent donor atom having available lone pair of electrons, which gives a partial double bond character to the donor metal sigma bond. This could be schematically represented as in Fig. 8.

(8)
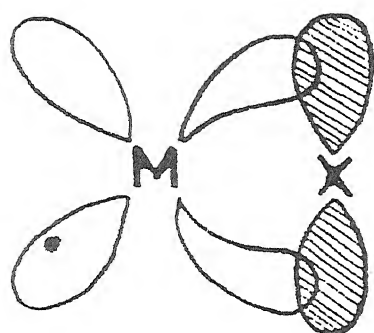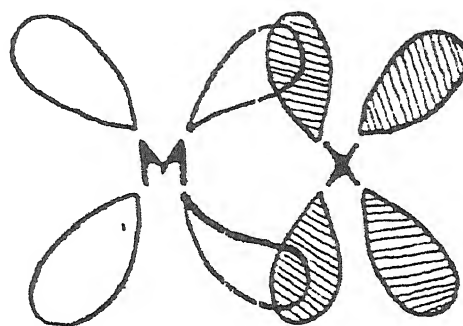
$d\pi$ - $p\pi$ interaction $d\pi$ - $d\pi$ interaction

Fig. 8

Organotellurium compounds

The first organotellurium compound, diethyl telluride, was synthesised by woehler in 1840. Since them many reports have appeared which deal with various aspects of organotellurium chemistry. The organic chemistry of tellurium up to 1974 has been exhaustively reviewed by Irgolic[16].

Methods of preparation of Te-C bonded molecules :

In most of the reactions tellurium metal, tellurium hydride, sodium-and other metal tellurides, tellurium tetrachloride and organic tellurium compounds have been used to synthesise Te-C bonded molecules. A short account of these methods is given below:

A. Elemental tellurium :

A number of organotellurium compounds are synthesised directly from elemental tellurium. The reactions resulting in the formation of the least one C-Te bond are summarized in (Fig.9).

B. Tellurium hydride :

There are a few recent reports of the use of tellurium hydride as a reagent to introduce tellurium in organic molecules[17,41].

C. Sodium and other alkali metal tellurides :

Alkali metal tellurides are easily alkylated by organic halides. Upon mixing stoichiometric amounts of diacetylenes with sodium telluride and hydrolysing the product, 2,5-disubstituted tellurophenes are isolated. With aliphatic alcohols at 300-150°, alkali metal tellurides give tellurols and tellurides (Fig.10).
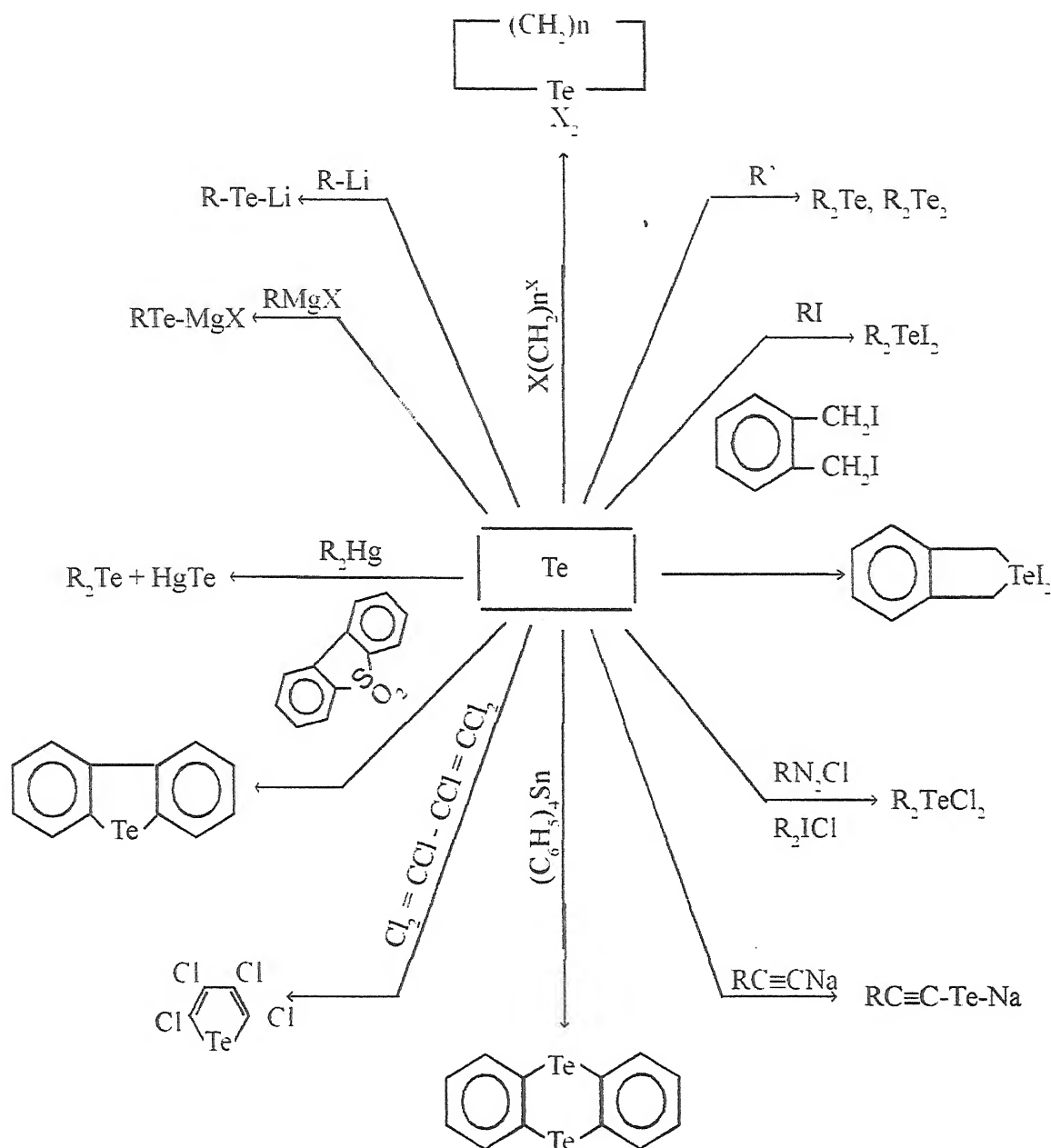
Fig.9

D. Tellurium tetrachloride :

There are a large number of reactions taking place between anhydrous tellurium tetrachloride and organic reagents which proceed with formation of molecules containing at least one carbon-tellurium bond (Fig.11).

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E. Organic tellurium compounds :

A general outline of the reactions of organotellurium compounds leading to the formation of additional carbon - tellurium bonds is given in Fig. 12.

$$R_2Te + 2MX$$

$\uparrow$ RX

ROH   2ROH

$$RTeH \longleftarrow \boxed{\text{Alkali Metal + Telluride}} \longrightarrow R_2Te$$

$$R-C\equiv C-C\equiv C-R$$

$$R \qquad R$$

$$Te$$

Fig.10

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RMCl$_2$ + RTeCl$_3$

RH   R

(RC$_6$H$_4$)$_n$TeCl$_{+n}$ ← RC$_6$H$_4$SMe$_3$ → R$_2$CCCOCH$_2$COCH-)$_n$
                                                        TeCl$_{+n}$

R$_2$TeCl$_2$,   RHgCl
R$_3$TeCl   R$_2$Hg

R$_2$TeCl$_2$,   RMgX
R$_3$TeCl

R$_3$TeCl, R$_4$Te,   RLi   →   TeCl$_4$
R$_2$Te,

(C$_6$H$_5$)$_n$TeCl$_{+n}$ Ph$_4$Sn
(n=1 or 2)   Ph$_4$Pb

O R
(RC-CH-)$_n$TeCl$_{+n}$

CH$_3$NO$_2$ O$_2$NCH$_2$TeCl$_3$

RC≡CR   R-C-Cl
          R-C-TeCl$_3$

(X- —)$_n$TeCl$_{+n}$

Cl
—TeCl$_3$

O$_2$NCH$_2$TeCl$_3$

Te
Cl$_2$

R$_2$MCl (M=In,Ga,Tl)
R$_2$CHRCOCH$_2$COCH$_2$R
CH$_2$=CH$_2$

Fig. 11

(13)
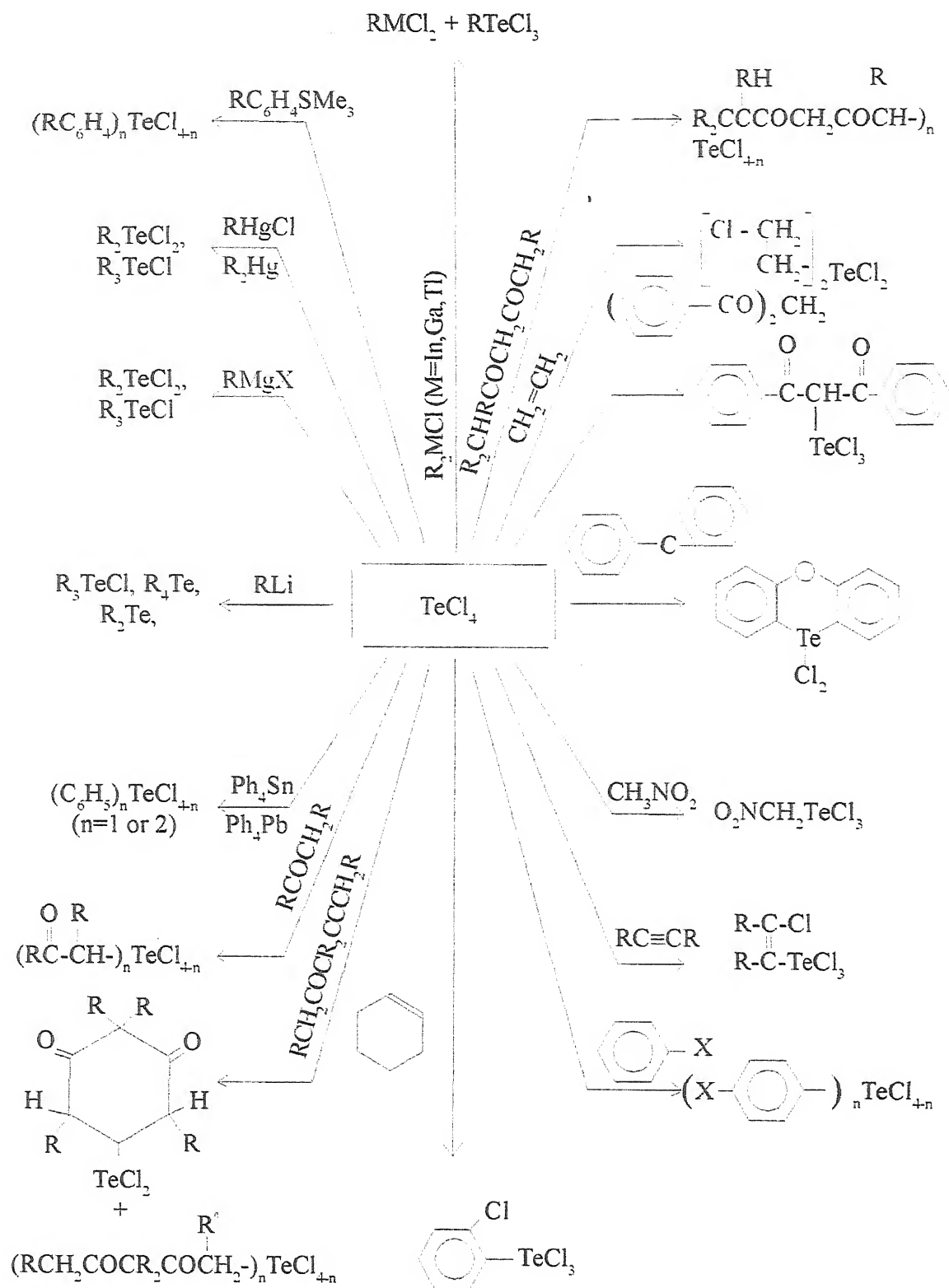
The book "the Organic Chemistry of Tellurium" by Irgolic covers the organotellurium literature during the time span from 1840, When Wohler reported the first organotellurium compounds, through 1971. The organotellurium chemistry after 1971 has progressed unexpectedly. In the preset investigation, a number of organotellurium compounds, have been prepared and characterise. It would, therefore, be appropriate to give a short account of the chemistry of organotellurium compounds before describing the details of the present investigation.

On the basis of oxidation states, the organotellurium compounds may be classified into four main headings :
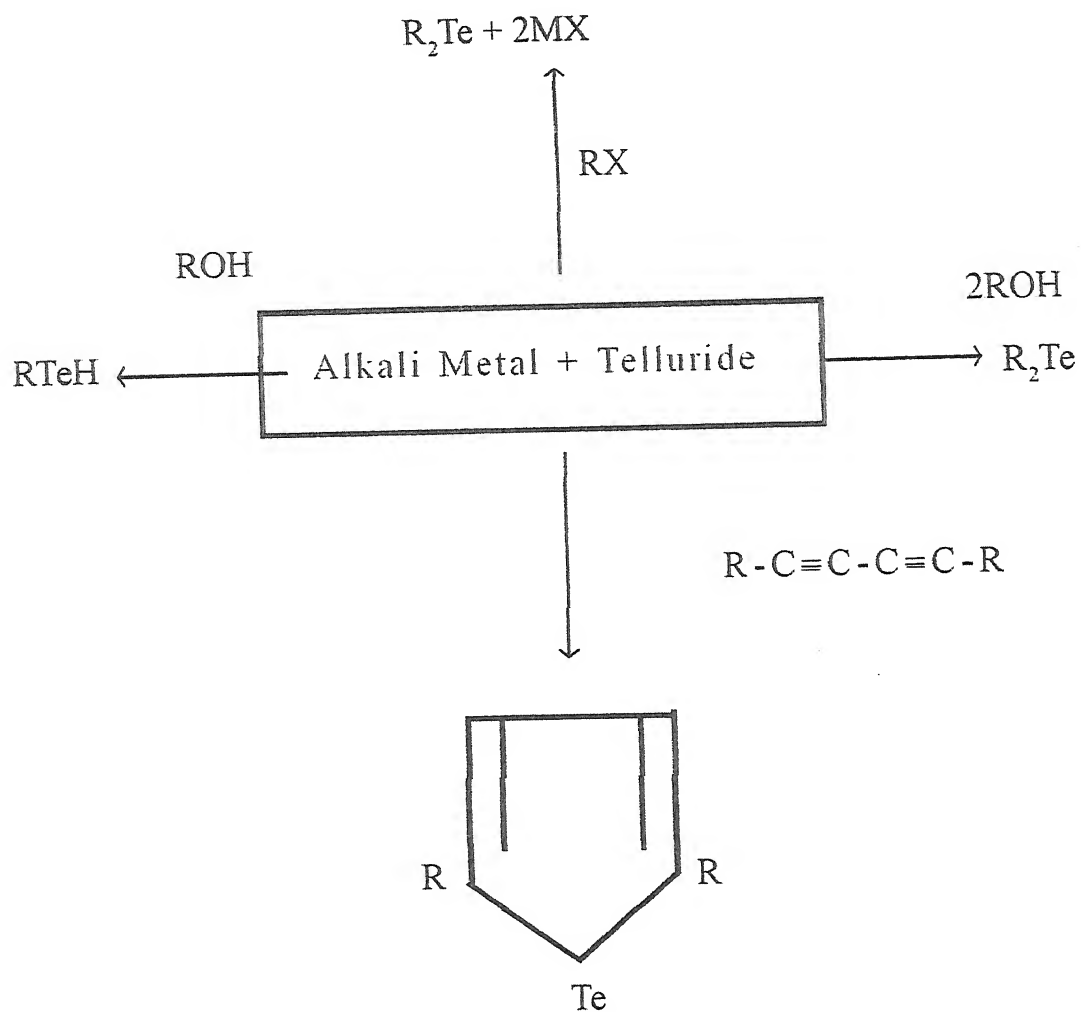
(i)   Oxidation state zero,

(ii)   Oxidation state two,

(iii)   Oxidation state four and

(iv)   Oxidation state six

(i) Compounds in oxidation state (0)

In 1973, first such compounds $[(C_6H_5)_3P]_2Te$ was prepared in 30% yield, when tellurocyanates reacted with triphenylphosphine in acetonitrile solution on presence of lithium perchlorate. This zero valent compound decomposed at $83-85^0c^{42}$. The structures of $[(Ch_3)_3P]_2Te$ and $[(CD_3)_3P]_2Te$ have also been suggested on the basis of IR and Raman spectra data[43].

(ii) Compounds in oxidation state(II)

These includes tellurols (RTeH), tellureny 1 compounds (RTeX), tellurides (R_2Te) and ditellurides (R_2Te_2).
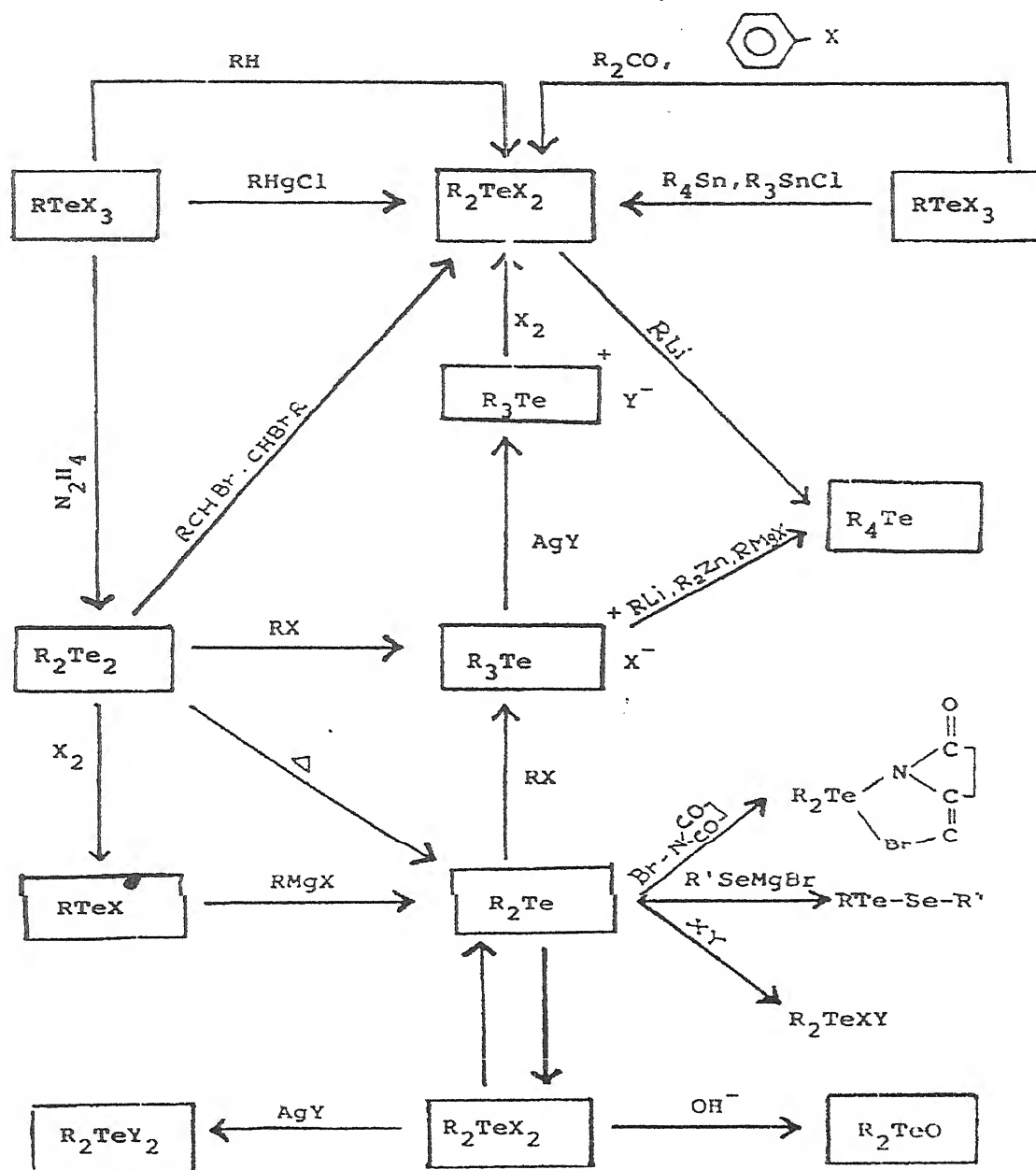
Fig. 12

Tellurols: Our knowledge about these compounds in limited owing to the exceedingly unpleasant odour , especially in case of the alky derivatives. How-

ever, methanetellurol and trideuteriomethanetellurol have been prepared by the hydrolysis of dimethyl detelluride[44]. Lederer reported that benzene tellurol reacts with mercuric chloride to yield C_6H_5-Te-$HgCl$[45].

Tellureny Compounds: Aliphatic RTeX are still unknown. With the exception of 2-napthyltellurium iodide, it has not been possible to isolate other aryl tellurium halides. However, in solution, aromatic derivatives can be prepared[46]. X-Ray structural analysis established the structure of 2-formylphenyl tellurium (II) derivatives as shown in Fig.13.

$$(X = Cl, Br, I, CN, SCN, SeCN)$$
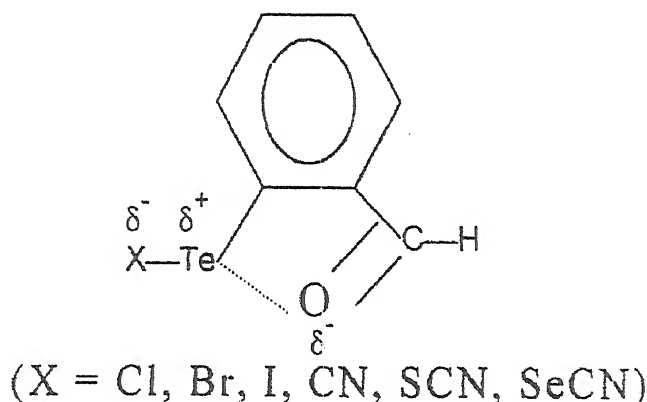
Fig. 13

PhTeCN has been prepared through reductive cyanation of aryltelluriumtrichloride and form the reaction of aryltelluriumbromide with KCN^{47}. The reactivity of 2 - napthyltellurium iodide has also been reported[48-49].

Tellurides: Synthesis and reactivity of diorganyltellurides are shown schematically in (Fig.14), which also includes several new routes for preparation of symmetrical[50-52]. and asymmetrical[53], [17], [54-57] tellurides. Several tellurides, with two
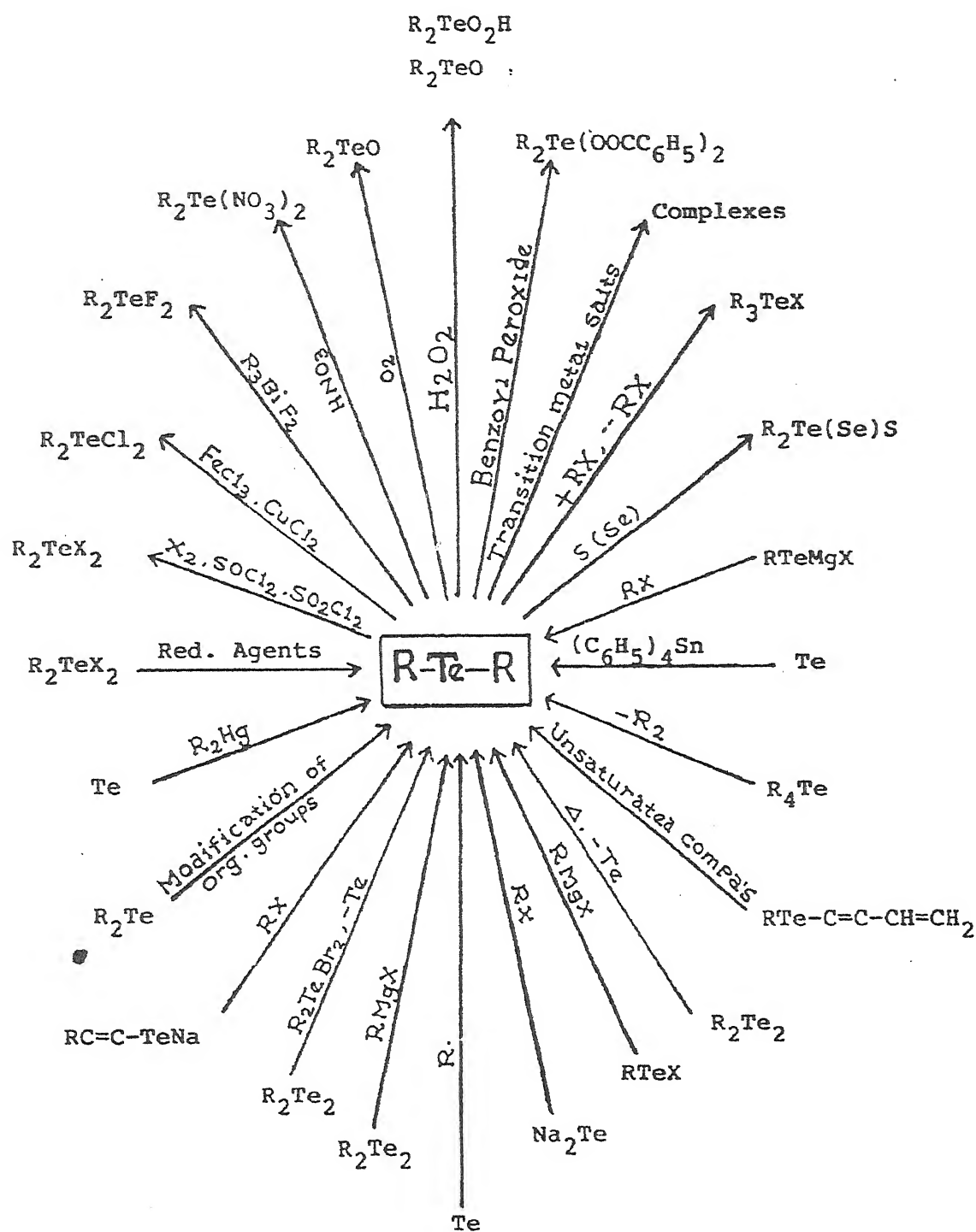
Fig. 14 Syntheses and reactivity of
diorganyl tellurides

tellurium atoms in a molecule have been synthesised by Seeback and Beck[58].

Some of the reactions which were carried out with such type of tellurides are

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schemed elow (Fig.15).

$$C_6H_5\text{-Te-CH}_2\text{-Te-C}_6H_5$$

with arrows:

Left arrow: RLi / THF, -78°C

Right arrow: $(t\text{-C}_3H_7)_2NLi$ / THF, -78°C

$C_6H_5\text{-Te-CH}_2Li$
+
$C_6H_5\text{-Te-R}$

$R=CH_3\text{-},C_4H_9\text{-},$
$t\text{-C}_4H_9$

$D_2O \quad C_6H_5\text{-CH}_2Br, THF - 78°C$

$C_6H_5\text{-Te-CH-Te-C}_6H_5$
D

$C_6H_5\text{-Te-CH-Te-C}_6H_5$
$|$
Li

$C_6H_5\text{-Te-CH-Te-C}_6H_5$
$|$
CH_2
$|$
C_6H_5
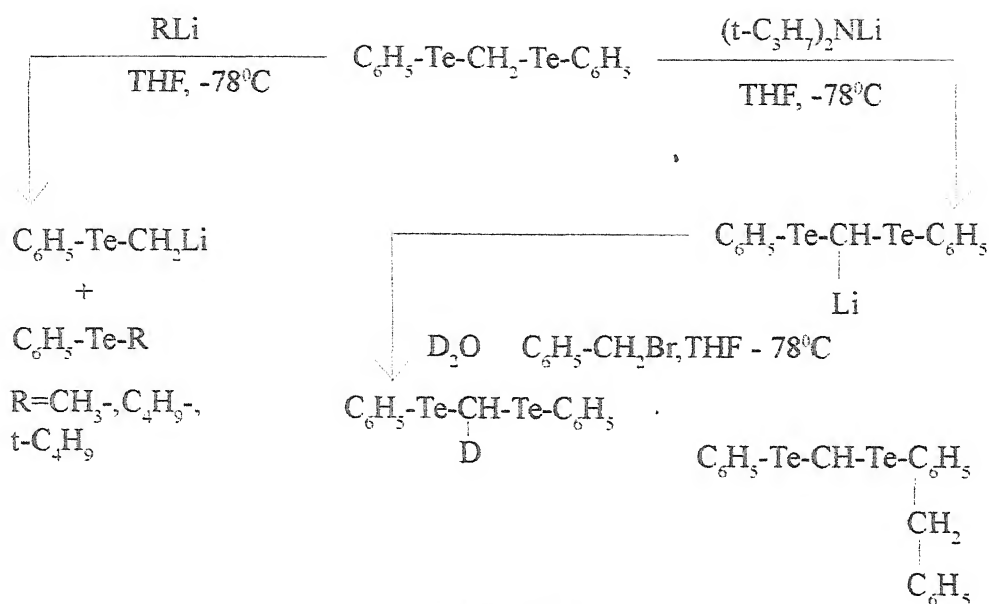
Fig. 15

The case with which bis (organo) telluriumdihalides are formed, lead to the investigation of the tellurides as dehalogenating agents[59]. Lederer prepared a number of adducts of diphenyltellurides and dialkyltellurides[60-61]. The structure of tellurides have been determined using UV, PMR and mass spectral data[62-64].

Ditellurides: The first unsymetrical diorganyl ditelluride, perfluorobutylpentafluoroethyl ditelluride, was formed in a reaction between tetrafluoro ethylene and $Te_4(AsF_6)_2$ or $Te_6(AsF_6)_2$[65]. Recently, some new symmetrical diarylditellurides have been reported [66-70]. All the ditellurides are orange to red solids except methyl derivatives. Fission of Te-Te bond is brought about by halogenolysis with the formation of corresponding organotellurium (II) halides. Thermally, ditellurides decompose of R_2Te and Te[71-72]. The struc-

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ture of bis(4-chlorophenyl) ditelluride has been determine by single crystal X-ray analysis[73] (Fig.16).
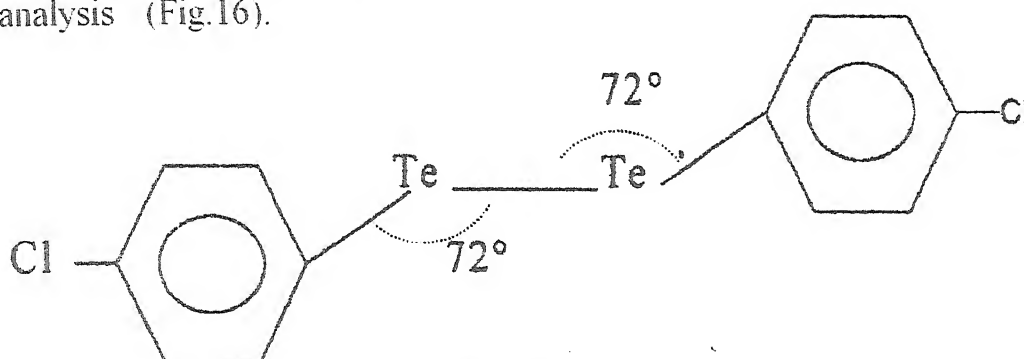
Fig. 16

2-alkoxy ethyl aryl tellurides $4\text{-}R^1C_6H_4TeCH_2CH_2R^2(R^1 = H,Me, R^2 = OMe, OEt)$ were obtained in 70-80% yield by the reaction of 1-bromo-2methoxy ethane or 1-bromo-2ethoxy ethane with arene telluralate anion. These telluride were converted to their corresponding $TeCl_2$ which on treatment with $NaOCH_2CF_3$ in CF_3CH_2OH medium gave the corresponding bis (2,2,2-trifluoroethoxides) in 70-80% yields [74].

$(2\text{-}RN{:}CHC_6H_4)_2Te$ (R = alkyl. aryl) were prepared in $\geq 70\%$ yield by condensing $(2\text{-}HCOC_6H_4)_2Te$ with amines. X-ray analysis of $(2\text{-}RN{:}CHC_6H_4)_2$ Te (R = o-MeOC$_6$H$_4$) showed one intramolecular Te $\longleftarrow$ N coordination (2.702 A^0) in crystal^{125}Te NMR spectroscopy showed a trans coordination process occurring via rapid cleavage nd formation of Te $\longleftarrow$ N bonds[75].

The ditelluro ethers $o\text{-}C_6H_4(TeMe)_2$ was prepared from $o\text{-}C_6H_4Br_2$ and LiTeMe in THF and $o\text{-}C_6H_4(TePh)_2$ was obtained similarly from $o\text{-}C_6H_4BrI$ and LiTePh. Synthesis of the o-Substituted telluro ethers $o\text{-}C_6H_4(TeMe)_y$ (Y = NMe$_2$,

PMe$_2$, AsMe$_2$, SbMe$_2$, OMe, SMe, SeMe and Cl) are also reported. The compounds have been characterized by mass spectroscopy by multinuclear NMR spectroscopy (^{1}H,^{13}C,^{125}Te) and by the preparation of derivatives. The trends in the ^{125}Te NMR chemical shifts are compared and comparison are also made with the ^{77}Se NMR chemical shifts in corresponding seleno ethers convenient synthesis for o-C$_6$H$_4$Cl (SMe) and o-C$_6$H$_4$Cl (SeMe) are reported[76].

The chloro (phenyl) trimethane selenourea Te(II) compounds were prepared in 69% yield by treating diphenylditelluride with trimethylene selenourea and chlorine in MeOH. The structure of this and bromo (phenyl) trimethne thiourea Te(II) were determined by x-ray crystallography[77].

Three coordinated Te(II) complexes of type (p-RC$_6$H$_4$Te-CH$_2$ NCSNHN = CR^{1}R^2) Cl (R = H, OH, MeO, R^1 = Ph, C$_6$H$_4$OH, R^2 = H, Me) were prepared by treating p-RC$_6$H$_4$TeCl$_3$ with H$_2$NCSNHN = CR^{1}R^2 in aq.MeOH molecular weight and conductivity measurement suggest that the Cl in these complexes is ionic. The I.R., ^{1}H and ^{13}C NMR data suggests that coordination of H$_2$NCS-NHN = CR^{1}R^2 is through S alone, probably giving three coordinates Te. The nature of Te-S bonding and the stability of complexes is reported[78].

Diarylditellurium p-RO-C$_6$H$_4$Te-TeC$_6$H$_4$OR-p(R = Me, Et) react with thiocyanogen in dry absorbtion MeOH at 110^{0}C to give unstable monoaryl Te (II)thiocyanate which were isolated as adducts with neutral M$^-$,O$^-$,OS$^-$ donor ligands for example thiourea, β-picoline, triphenylarsene oxide reaction of

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diarylditellurium with ICl, IBr gave p-ROC$_6$H$_4$ TeX (X = Cl, Br, I)[79].

Te (S$_2$COEt)X have been synthesised by Te (S$_2$COEt)$_2$ with TeCl$_4$,CuCl$_2$ or CuBr$_2$.The X-ray crystal structure of Te (S$_2$COEt) Br shows. It is composed of left and right handed helices formed from common sharing (B$_1$ bridges) of planner Te (S$_2$ COEt) Br units. The C-O bond length is the shortest so far observed in metal xanthates[80].

The IR and Raman spectra of crystal samples of halo (ethylene thiourea) phenyl tellurium(II) (halo = Cl, Br, I), halo (ethylene selenourea) phenyl tellurium (II) halo-Cl, Br , phenyldithiocyanato and phenyldiselenocyanato tellurate(II) ions, were recorded below 500 cm^{-1}. From these data, the two fundamental stretching frequencies connected with the approximate linear X-Te-Y linkage were assigned. These frequencies were compared with those obtained from a simplified force constants[81].

The porphyrin Fig.(17) was prepared from 2, 5-bis (phenylhydroxy methyl)tellurophene by reaction ewith pyrrole followed by cyclocondensation reaction with 2, 5-bis (phenylhydroxy methyl) thiophene[82].
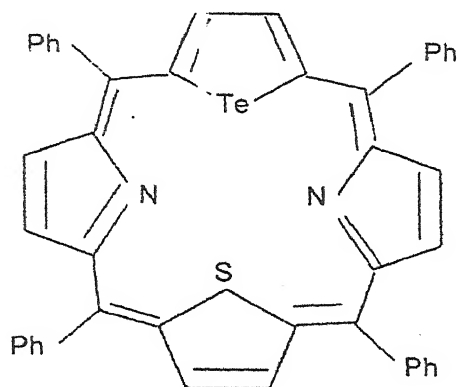
Fig. 17

(21)

Successful reduction of benzene derivatives $p\text{-}Cl_3TeC_6H_4R(R=SiMe_3)$ with $Na_2S_2O_5$ and Cu affords ditelluride $p\text{-}RC_6H_4$ Te_2C_6 $H_4R\text{-}p$ and telluride $(p\text{-}RC_6H_4)_2$ Te respectively. Reactions of $p\text{-}RC_6H_4TeC_6H_4R\text{-}p$ and $(p\text{-}RC_6H_4)_2$ $(R= SiM_3)$ with halogens results in oxidation of'Te and the formation of the corresponding σ - trelluranes. Alkylation of ditellurophenolates anion following upon reduction of $RTeCl_3$ furnishes p-bis (alkyltelluryl) benzenes[83].

The ^{125} Te mossbaur spectra for $(CF_3)_2$ Te and $(C_6F_5)_2$ Te exhibit significantly larger quadrupole splittings than those of Me_2 and $Ph_2Te(CF_3)_2TeX_2$ and $(C_6F_5)_2TeX_2$ (X=F,Cl, Br) have consistently smaller quadrupole splittings than Me_2TeX_2 and Ph_2TeX_2. These observations are consistent with the greater electronegativity of CF_3 and C_6F_5 ligands. The ^{125}Te NMR chemical shifts of $(C_6F_5)_2$ and its dihalides show a consistent trend to more positive values (increased deshielding as the electronegativity of the ligands attached to Te increases), however, for $(CF_3)_2$ Te and its dihalides a more complex pattern is observed which is explained by changes in the mean electronic excitation term in the Ramsay paramagnetic shielding term[84].

^{125}Te NMR spectra of Te(II) complexes contained dithiolene on others unsaturated-1, 1-dithio-1, 1-thioseleno or 1, 1-diseleno ligands are reported. According to their chemical shift value, the complexes can be divided into groups will separated by several hundred ppm[85].

^{125}Te chemical shifts of $Te(S_2)_2Te(NR_2)_4$ (R=Et,CHMe$_2$, iso-BuPhCH$_2$),

(22)

(R$_2$N=N-pyrrolyl) and Te(S$_2$CNEt$_2$)X (X = Cl,Br,I,NCS) are separated by~1400 ppm. When R is an alkyl group, the electronic configuration as contribution to the chemical shift appear to be very small for both oxidation states of Te. The chemical shift of these compounds display a positive temperature dependence consistent with the major contribution arising from paramagnetic shielding. The preparation of Te(S$_2$CNEt$_2$)$_2$ from Te(Et$_2$NCS$_2$)$_2$ and that of Te(S$_2$CNEt$_2$)$_3$I from Te(S$_2$CNEt$_2$)$_3$Cl and KI are reported addition of [(Me$_2$CH)$_2$NCS]$_2$ and (Et$_2$NCS)$_2$ to Te(S$_2$CNEt$_2$)$_2$ and CdCl$_3$ gave mixture Te(S$_2$CNEt$_2$)$_2$[S$_2$CN(CHMe$_2$)$_2$]4-n (n = 0-4), Te(S$_2$CNR$_2$)$_4$ disproportionate to Te(S$_2$CNR$_2$)$_2$ and (R$_2$NCS$_2$)$_2$[86].

The nature of the bonding to Te in the phosphine complexes R$_3$PTe and (R$_3$P)$_2$Te and in tellurocyanates, TeCN$^-$, ArTeCN$^-$, ArCH$_2$TeCN and ArTe(X)CN (X = Cl,Br,I) was studied by [125]Te solution NMR spectroscopy at ambient temperature and by[125] Te mossbaur spectroscopy at 4.2K. No evidence was found for multiple bonding to Te in either solution or the solid state. The phosphine complexes R$_3$PTe give [125]Te NMR shifts of-837,-497 ppm (Me$_2$Te) at [125]Te quadrupole splitting of 10-12mmS^{-1}. The TeCl$^-$ ion has a [125]Te NMR shift of -509 to -569 ppm dependent on solvent and conversion, ArTeCN and ArCH$_2$TeCN shifts of +570-580 ppm and the halide derivative ArCH$_2$Te(X)CN$^-$,shifts of -586 to 604ppm Te. [125]Te mossbaur quadrupole splitting of TeCN$^-$ is 12mmS^{-1} of ArTeCN and ArCH$_2$TeCN is 13.7-14.1mmS^{-1} of ArCH$_2$Te(X)CN, X=Cl, is 14.5 mms^{-1}, ArCH$_2$Te(X)CN, X = Br, is 13.8 mms^{-1} and ArCH$_2$Te(X)CN, X = I is 14.0 mmS^{-1} [87].

(23)

The chloro and bromophenyl (tetramethylthiourea) tellurium (II) are mono-clinic, space group $p_{21/n}$, z = 4 chlorophenyl (tetramethylthiourea) Te (II) has a = 7.7301, (b) b = 12.6097 (8) , c = 15.2179 (9)A^0 and β = 99.011 (6)^0 R = 0.040 bromophenyl (tetramethylthiourea) Te(II) has a = 7.7306 (b) , b = (12.8673) (h), c = 15.4239 (II) A^0 and β = 99.737 (8)^0 R = 0.044 chlorophenyl (trimorpholinephosphine selenide). Tellurium (II) has a = 9.2467(12), b = 18.9217(16), c = 13.396(12)A^0 and β = 99.852(9)^0 R = 0.037. The first two compounds are isomorphous as are also the last two, the fourth complexe are 3 coordinated T- shaped. In a direction nearby perpendicular to Te-C bond. Te is bonded to halogen atom and in transposition to the halogen atom to a tetramethyl thiourea S on a tromorpholylphosphine selenide Se atom. The three centre systems X- Te- X where X is halogen, are nearly linear and At coordinates, bond angles and bond lengths are reported[88].

The bis(2-hydroxyethyl) dithiocarbaomato tellurium (II) i.e., $Te(C_5H_{10}NO_2S_2)_2$ is monoclinic space group P21/C with a = 11.303 (S), b = 5.543 (1), c = 28.724 (5) A+ and β = 100.30(1)^0 Dm = 1.76 Dsc = 1.83 mgm^{-3} d (experimental) = 1.76 and d (calculated) = 1.83 for z = 4 final R = 0.066 for 1314 unique observed reflections. Each Te atom is bonded to all 4S atoms of the 2 ligands forming an asymmetrical planner complex with Te-S bond dis-tance of 2.527 (7) - 2.793 (8) A^0. The molecules are linked in pairs by a short intermolecular contact Te-S (2) of 3.296 (A)^0 indicating a tendency towards 5 coordination around Te-two of the four EtOH groups in the molecule show a disorder of orientations[89].

The tellurium (II) ethyl xanthate with 4,4-bipyridyl is monoclinic space group P21/c with a = 9.0249 (9), b = 13.211 (2), C = 14.347 (2) A^0 And β = 102.3 (2)^0 d (expt L) = 1.77 and d(calculated) = 1.780 for Z = 4 final R = 0.053. Crystals of the adducts consist of molecular binuclear species. Each of Te had planar pentagonal coordination by 4S from two bidentate xanthate ligands and one of the bipyridine[90].

The trans bis 2(3H)-benzimidazolethione bis(thiourea) tellurium(II) chloride i.e., $Te(CH_4N_2S)_2 (C_7H_6N_2S)_2Cl_2$ is monoclinic space group Pzl/C with a 6.623(1), b = 11.3873(3), c = 16.085(3) A^0 and Dc = 1.787 for z = 2. The final R = 0.029 and R$_w$ = 0.027 for 2068 reflections. The Te lying at the crystallography centre of symmetry is bonded to a thiourea 5 atoms and 2 benzimidazole thione 5 system (atoms) in a trans square planar arrangement. The TeS$_4$ group has the dimensions Te-S(1) 2.694(2) Te-S(2) 2.685(1) A^0 and S(1) A^0 and S(1) – Te-S(2) 89.4(1)[91].

$Te(tu)_2(ClO_4)_2$ (tu = thiourea is triclinic, space group Pl with a = 15.35, b = 11.97, c = 6.01A^0, α = 90.1, β = 91.0 and γ = 108.0^0 2=2 final R = 0.032 $Te(dmtu)_4Cl_2$(dmtu = 1,3-dimethy thiourea) is monoclinic space group P21/n with a = 13.70, b = 9.05, c = 10.91A^0 and β = 101.6^0 Z = 2 final R = 0.025). In both the complexes the Te is bonded to four 5 atoms in a planar arrangement which is considerable distorted in the perchlorate but nearly regular in the chloride, to explain the structural and [125]Te, mossbaur spectroscopy results a bonding model involving lone pair with S and p characteristics then proposed[92].

(25)

The bromo (o-ethylaxanthato) tellurium(II) is monoclinic space group P21/C with a = 10.636(1), b = 6.030(1), c = 13.364(1)A^0 and β = 103.32(1)^0 d (expt) = 266 and d(calculated) = 2.617 for Z = 4final R = 0.077 (R$_w$ = 0.072) each Te is bonded to 2S atoms of the xanthate ligand and 2 Br atoms with each Br atom bonded to another Te atom. The Te and Br atoms adopt a helical structure with a pairs of Br and Te atoms forming the repeat unit[93].

X-ray data for the bis(thiobenzoate-5) tellurium i.e., $C_{14}H_{10}O_2S_2Te$ indicate that Te is covalently bonded to S. There are weak secondary interactions between Te and O which complete in S_2O_2 coordination around Te. The CO and CS distances of I are normal and agree with published values. The two pH rings are planar with the C atoms derivating from the plan by less than 0.01(1)A^0. The average CH distance is 0.86 (4) A^0 and the average C-C-H angle is 120(7)^0 [94].

Te(II) 2-oxazollidinene derivatives are useful as intermediate for drugs of animal and human are prepared by treating olefins with carbamates esters in the presence of Lewis acids and ArTe(O)OCR (Ar = Un) substituted aryl haloalkyl as mediators. Cis 4-octene $H_2NCOOCF_3$ and BF_3Et_2O were added to a solution of $PhTe(O)COOCF_3$ in dichloroethane and the mixture was refluxed for 12 hours to give 85% cis-4,5-di-n-propyl-1,3-oxazolidine-2-one[95].

Ethynylepichlorohydrin (R^1 = alkyl, H, Ph, tetrahydropyranyloxymethyl) were treated with Na_2Te to give telluriophenomethanols[96].

$O^-(Me_3Si)_2C_6H_4$ reacted with two equivalent $TeCl_4$ in O-$Cl_2C_6H_4$ to give 66% o-$(Cl_3Te)_2C_6H_4$, which was reduced with $Na_2S_2O_5$ to give the polymeric ditelluride $(o$-$C_6H_4Te_2)_n$. Further reduction of 6-$C_6H_4Te_2$ with $NaBH_4EtOH$ and cyclization of the resulting di-Na derivative with CH_2Br_2 gave 16% benzoditellurole which gave the tetra bromide with Br[97].

The compound fig.18.(R = H, M = M^1 = Te,Se, R^1 = p-$MeOC_6H_4$, p-$EtOC_6H_4$ p-MeC_6H_4, R = Me, M = Te, M^{1}Se M= Se M^1 = Se R^1 = p-MeO-C_6H_4) via an intermediate singlet benzyne, have been synthesised[98].
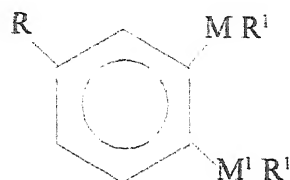
Fig. 18

Moss-bauer data are reported for a number of heterocyclic compounds contend Te (Fig.19). The influence of the bulky-2-biphenyl ligand on the mossbauer parameters of diaryltellurium dihalides and aryl tellurium trihalides was also investigated[99].

Fig. 19

Elemental Te reacted with C_2H_2 and PhI in HMPA-H_2O contained $SeCl_2$ and KOH in an autoclave 100-120 and 10-12 atoms to give 20% PhTeCH = CH_2(I), 17% $(CH_2$=$CH)_2$ Te and 20% Ph_2TeI information was reduced to <1%

(27)

with PhBr instead of PhI or in the absence of $SnCl_2$ and was inhibited by added hydroquinone or with PhCl. . An anion radical mechanism was proposed[100].

Solution of disodium ditelluride in DMF react with the solvent to give small yield of the unusual ditelluride $[Me_2NC(O)]_2Te$. This molecule exhibit interesting photochemical behaviour and was experimentally characterised and its crystal structure was determined[101].

XPS (ESCA, electron spectroscopy for chemical analysis) of oxatellurolylium halides Fig.20 (R = halo, R^1=alkyl, aryl, R^2=aryl) and dioxatellurapentalenes (same R^1,R^2) have shown them to be Te(II) compounds. When their $Te3d_{5/2}$ binding energies are compared to those of te(II) models. The oxatellurolylium trihalides (same R^1,R^2) and, by extension, the dioxatellurapentalene dihalides (R = H, Cl) $Te3d_{5/2}$ binding energies consistent with Te(IV) when compared to te(IV) compounds. Changes in XPS binding energies which result from subsituent changes in the carbon framework are similar in magnitude to changes, from substitution in the electronegative ligands attached to Te, this makes quantitative assessment of the effect of higher order bonding on the electronic environment at Te difficult usingh the $Te3d_{5,2}$ binding energies.

(I)   (II)   (III)

(IV)   (V)

Fig. 20

(28)
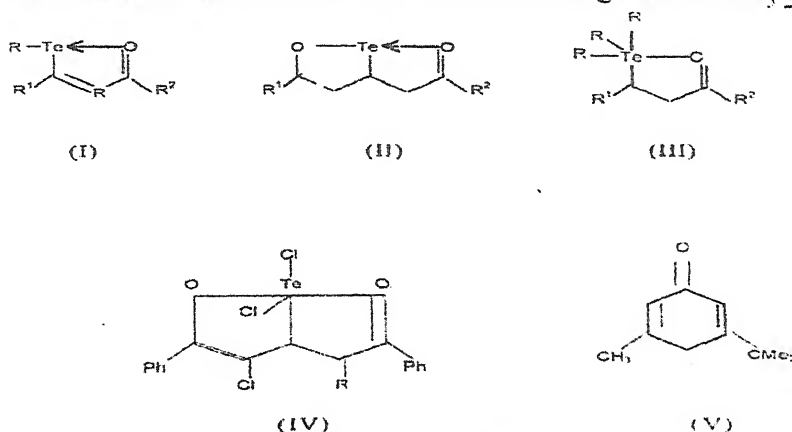
The O$1s$ electrons of (I-III) have higher binding energies than model compounds (V) (X = Te, TeCl2) suggesting that partial bonding (linear, there is centre four electron bonding) exists between the Te halides. The Te and the one oxygen (RTe....O) while the XPS data show the oxygen atoms to be donating electrons in the 3C-4e bonds, the ^{125}Te NMR chemical shifts show deshielding as three centre four electron
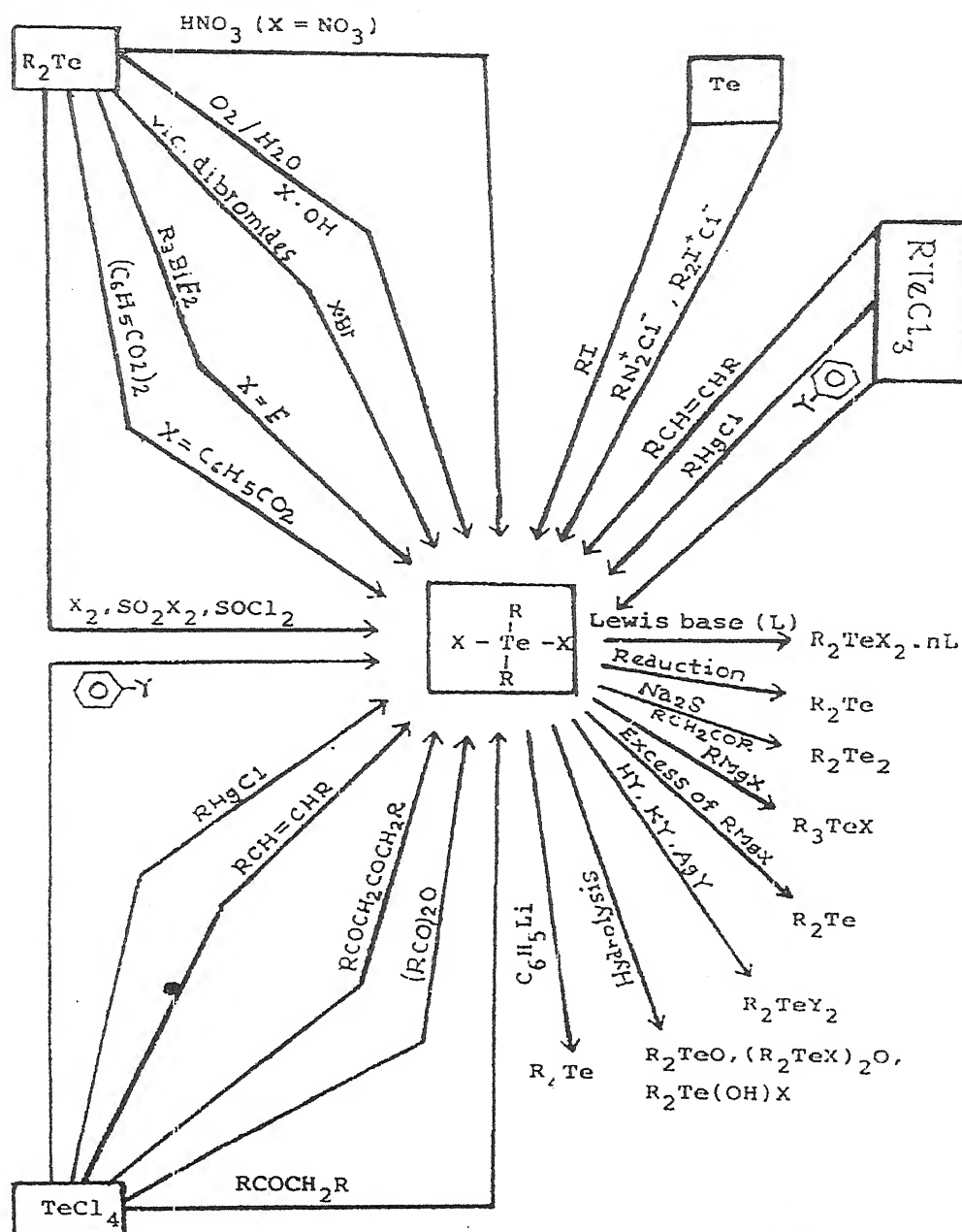
Fig. 21 : Synthesis and reactivity of R$_2$TeX$_2$

(29)

Fig. 22 : Synthesis and reactivity of RTeCl₃

bonding increase with dioxatellurapentalene (II) ($R^1 = R^2 = Ph$) as one limit

with a symmetrical structure three centre four electron bond and tellurapyranone

(V) [X = Te(VI)] as the other unit with no bond between Te and O. The ^{125}Te

(30)

NMR chemical shifts move subsequently down field from VI to β (tellurophenyl) butenoate ester (I) (R = Ph, R^1 = Me, R^2 = OEt to (I) (R = iodo to (I) (R = Br to (I) (R = Cl) in the Te(II) series and Te(IV) respectively. The XPS and ^{125}Te NMR structure of these compounds are first systematic studies of this type of compounds as, the data suggests that ^{125}Te NMR chemical shift are sensitive to the geometry of the complexes, the oxidation state of Te and electronic environment of Te[102].

(iii) Compounds in oxidation state (IV)

Most common compounds of tellurium have metal in the oxidation state (IV). Organotelluriumtrihalides ($RTeX_3$), dioganotelluriumdihalides (R_2TeX_2), triorganotellurium halides (R_3TeX), tetraorganotellurium (R_4Te), organotetrahalotellurates $M^+[RTeX_4]^-$ and $M_2[R_2TeX_4]$[103,104] and telluroxides (R_2TeO) come under this category.

$RTeX_3$, R_2TeX_2 and R_3TeX generally behave as Lewis acids of class 'b'. Organotelurium trihalides and dioganotellurium dihalides on reduction yield R_2Te_2 and R_2Te respectively. The hydrolysis product of aryltellurium trihalides is tellurinic acid halide, RTe(O)X, in which tellurium atom is tetracoordinated in a trigonal bipyramidal structure. The following scheme describes the hydrolysis of diorganotellurium dihalides:

$$
R_2TeX_2
\begin{cases}
\xrightarrow{H_2O} R_2Te(OH)X \text{ or } (R_2TeX)_2 \\
\xrightarrow{Ag_2O/H_2O} R_2Te(OH)_2 \\
\xrightarrow{NaOH,NH_3} R_2TeO
\end{cases}
$$

(31)
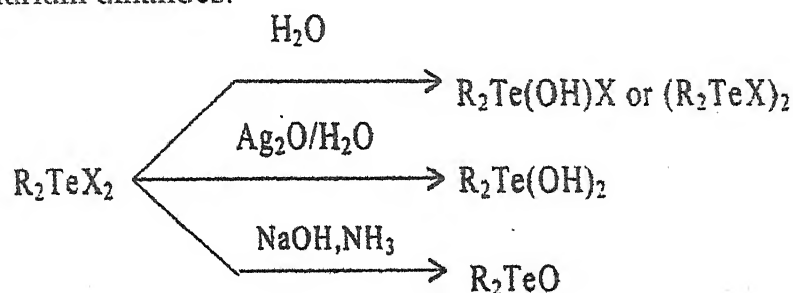
The reactivity of organotellurium trihalides when they condense with activated organic compounds with the formation of hydrogen halide and bis(organo) tellurium dihalides decrease in the order Cl > Br > I. $RTeX_3$ react with various organometallic derivatives of Hg, Sn, Pb, Si, Ga, In and Tl yielding R_2TeX_2 and their organometallic derivatives. Synthesis and reactivity of dihalides and trihalides are summarized in(figures.21 and 22) respectively.

On the basis of X-ray determination, R_2TeX_2 derivatives have been assigned a structure shown in Fig.23[105,108].
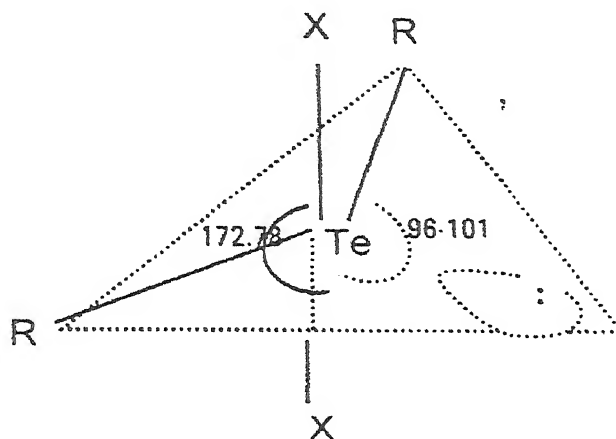
Fig. 23 Structure of trigonal bipyramidal

The tetrakis (dialkyl dithiocarbamato) tellurium(IV) are highly effective. Thermal antioxidants and melt stabilizers for polypropylene and converted to the bis(dialkyl dithiacarbamato) tellurium(II) complexes[109].

$Me_2Te(S_2COR)_2$ (R = Me, Et, Me_2CH) are obtained by reaction of Me_2TeI_2 with freshly prepared sodium xanthates. Another preparative method is the insertion of CS_2 into dimethyl tellurium bis(alkoxides). The X-ray analysis of

(32)

$Me_2Te(S_2COMe)_2$ shows that in the crystals the molecule has a four configuration around Te^{110}.

$TeX_4.L$ (X = Br,Cl,L=tetramethyl and tetraethyl dithioxamides) were prepared by the addition of $CH_2Cl\text{-}CH_2Cl$ solutions of TeX_4 to the ligands. The adducts were characterized by IR and UV spectra. The spectral measurements suggest octahedral structure with coordination through the S atoms. However, the distinction between bridging or bidentate moieties could not be made[111].

Reactions of $PhTeCl_3$ with (S_2CNEt_2), $(S_2P(OEt)_2)^-$ and $(S_2COEt)^-$ in solution were studied by variable temperature^{125}Te, ^{31}P, and ^{13}C NMR spectroscopy which show the formation of a variety of mixed ligand species; some of which were subsequently isolated. $MeTe$ (I)(S_2CNEt_2) (I) formed by oxidative addition of MeI to $Te(S_2CNEt_2)_2$ also provides a useful way to the synthesis of mixed ligand species, but in general the products are less stable than the pH analogous. Solvent dependent intramolecular exchange processes were observed for the alkyl and aryl series. The crystal and molecular structure of all mixed ligand complexes and $PhTe(S_2CEt_2)$ $(S_2P(OEt)_2)$ have been also determined[112].

$Ph_2Te(S_2(COR))_2$ and telluracyclopentane-1, 1-bis(alkyl xantahates) (R = Me, Et, CHMe$_2$) are obtained by reaction of Ph_2TeCl_2 or tellura cyclopentane-1, 1-diiodide with $ROCH_2Na$. The insertion of CS_2 into organotellurium bis (alkoxides) is only successful in the case of the cyclic compounds. The prod-

(33)

ucts decomposition on heating to Ph_2Te or telluracyclopentane and $ROCS_2S_2COR$[113].

$R_2Te(S_2CNR_2^1)_2$ (R = Me, Ph, R^1 = Me, Et, $CHMe_2$, cyclohexyl, Ph) were prepared from Me_2TeI_2 or Ph_2TeCl_2 and $R_2^1NCS_2Na$ from R_2^1NH, CS_2 and Me_2TeI_2 or Ph_2TeCl_2 by several other methods. Products of Me_2TeI_2 with $NaS_2CNMeCH_2CH_2NMeCS_2Na$ were obtained as polymers. Decomposition of $R_2Te(S_2NR^1_2)_2$ gave R_2Te, $R^1_2NCS_2S_2CNR^1_2$ and other products [114].

Ph_3TeOR (R = Me, Et, $CHMe_2$,) were obatained by treating Ph_3TeCl with RONa-ROH. Ph_3TeS_2COR were obtained from Ph_3TeCl and NaS_2COR from Ph_3Te OR and CS_2, Ph_2TeS_2CSR were prepared from Ph_3TeCl and NaS_2CSR[115].

Preparation and structural aspects of perchlorate complexes of Te(IV) with $RR^1NCS_2^-$, (R = R' = Me, Et, Ph, $CHMe_2$. PR^1N = piperideno morpholino) are reported[116].

A number of dithiacarbamate derivatives $Ph_2Te(S_2CNR_2)_2$ (R = Me,Et) and $Ph_2TeCl(S_2CMR_2)$ (R = Me, Et, $CHMe_2$) were prepared and characterised initially by analysis and vibrational spectroscopy. The crystal structures were determined so that the effect of the change in the nature of R and the presence of a Cl atom could be compared. The dithiacarbamate groups are monodentate (or anisobidentate) and the geometry about Te is consistently that of a dis-

torted sawhorse structure. Examples of both inter and intramolecular Te-S interactions are observed as well as an intermolecular Te-Cl interaction. The crystal structure of (R = Me) and (R = Et, CHMe$_2$) were determined. NMR spectra are not simple and indicate that several species are present in solution[117].

Ph$_2$TeS$_2$CNR$_2$ (R = Me, CHMe$_2$Ph) were prepared on heating Ph$_3$TeCl with R$_2$NCS$_2$Na. Ph$_3$TeS$_2$CNMe, CH$_2$CH$_2$NMeCS$_2$TePh$_3$ was similarly prepared . Ph$_3$TeS$_2$CNR$_2$ (R = Me) was also obtained from Ph$_3$TeO$_2$CNMe$_2$ and CS$_2$ thermal decomposition of Ph$_3$TeS$_2$CNR$_2$ gave R$_2$NCS$_2$Ph and Ph$_2$Te[118].

RTeX$_2$[S$_2$P(OR^1)$_2$] and R$_2$Te [S$_2$P-(OR^1)$_2$]$_2$ (R = p- MeOC$_6$H$_4$, Ph, R = Me, Et, CHMe$_2$; X = Cl,Br) were prepared in 56-57% yields from the NH$^+_4$ and Na salts of dithiophosphoric acid and the appropriate aryl tellurium trihalide or diaryl tellurium dichloride in CS$_2$ and were characterized by elemental analysis with proton NMR, I.R. and Raman spectra[119].

The crystal structure of [p-MeOC$_6$H$_4$TeBr$_2$(S$_2$P(OMe)$_2$] and Ph$_2$Te[S$_2$P(OMe)$_2$]$_2$ were determined in [p-MeOC$_6$H$_4$TeBr$_2$.S$_2$P(OMe)$_2$]. The dithiophosphate group is bidentate while in [Ph$_2$Te S$_2$P(OMe)$_2$]$_2$. it is monodentate in first compound the geometry around Te is that of a distorted square pyramidal, whereas in second compound it is that of a distorted sawhorse structure. In both cases a distorted octahedral confirmation about Te is completed[120].

(35)

$TeCl_4L_2$ (L = substituted thiourea) were prepared and characterized by elemental analysis, electrical conductivity, thermal analysis, I.R. and NMR spectral methods. The complexes are octahedral monomers with S-coordinated ligand[121].

Diphenyl selenium(IV) bis(O, O'-dialkyl dithiophosphates) $Ph_2SeS_2P(OR)_2$ (R = Et, $CHMe_2$, CH_2CHMe_2) diphenyl selenium(IV) bis(O, O'-alkylene dithiophosphates)$Ph_2Se(S_2POR''O)_2$ (R'' = $CH_2CMe_2CH_2$, $CHMeCH_2CMe_2$), $PhTe[S_2P(OCHMe_2)]_3$ and organotellurium(IV) tris(O, O' alkylene dithiophosphates) $RTe(S_2POR''O)$ (R = Ph, p-$MeOC_6H_4$, R = $CH_2CMe_2CH_2$) have been prepared and characterized from physicochemical and spectral (IR, ^1H and $^{31}PNMR$) studies. The results indicate a pseudotrigonal bipyramidal geometry around the selenium atom where the four position are accepted by the two Ph and two dithiphosphate ligands and the remaining one vacant position is occupied by a lone pair of electrons[122].

In the reaction of 3,3-bis (chloromercuric-2, 4-pentane dione [$(HgCl)_2L$]) with $TeCl_4Ph_2TeCl_2$ or Ph_3TeCl replacement of one HgCl group by a Te moiety gives $Cl_3TeLHgCl_2.C_4H_8O_2.Ph_2 Te(Cl)LHgCl$ and $Ph_3TeLHgCl$ respectively. The I.R. and H^i NMR data indicate that Te is bonded to C_3 carbon of acetyl acetone. In solution the compounds appear to ionize into Cl^- and an organometallic cation in which Hg seems to be involved in second interaction with the carbonyl groups. Far I.R.and mass spectral data suggest that Hg-O interaction is significant in solid structure or state[123].

(36)

The complexes $[R_2Te(p\text{-}OC_6H_4CHO)_2]$ (R = Ph, Me, $p\text{-}eOC_6H_4$, biphenylene)have been prepared by the reaction of $R_2Te(OMe)_2$ with salicylaldehyde. It react with haloacetic acid R^1COOH ($R^1 = CF_3$, CCl_3, $CHCl_2$, CH_2Cl) to give mixed ligand complexes $[R_2Te(p\text{-}OC_6H_4CHO)O_2CR^1)]$[124].

$Ph_3Te(RCOH;CR^1O)$ (R = Me, Ph,CF_3 R^1 = Me, Ph, CF_3, 2-thienyl) were prepared. The I.R., ^1H and ^{13}C NMR and mass spectra were discussed in conjunction with molecular weight and constant data, weak coordination of the diketone to the Te atom is common structural feature[125].

The reaction of (AcAc) with $RTeCl_3$, R_2TeCl_2 and R_3TeCl (R = Ph, 4-HOC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 3-Me-4-HOC_6H_3, 3,4-$(HO)_2C_6H_3$), have been investigated. $RTeCl_3$ gives $RTe(C_5H_4O_2)$ type derivatives but $RTeCl_2$ and R_3TeCl do not react even on prolonged refluxing in the presence of anhydrous $AlCl_3$. The structural features of the new acetyl acetone derivatives $RTe(C_5H_4O_2)Cl_2$ have been explored by I. R., NMR spectroscopy. The effect of phenyl ring substitution of the keto-enol tautomerism of $RTe(C_5H_4O_2)Cl_2$ has been found to be minor. The bond formation between Te and C-1 or AcAc and intramolecular secondary interaction between the oxygen of AcAc and Te have been obtained from the spectral data[126].

Diorganotellurium (IV) bis (β-diketonates) of the formula $R_2Te(acacH)_2$ (R = CH_3, C_6H_5, $p\text{-}CH_3OC_6H_4$) (acac H = 2,4 pentanedione) and $R_2Te(dpm)_2$ (dpmH = 2,2,6,6-tetramethyl heptane-3,5-dione) have been prepared by the

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reaction of $R_2Te(OMe)_2$ with (acacH) and (dpmH) in anhydrous condition. $R_2Te(acac)_2$ reacts with halocarboxylic acid (R'COOH) (R' = CF_3, CCl_3, $CHCl_2$, CH_2Cl) to give mixed ligand compound of the type $R_2Te(acac)(R'COO)$. A weak coordination of the β-diketone group with tellurium atom in solid state is concluded. The geometry around the central tellurium atom is suggested in the basis of physicochemical studies[127].

Tellurium dioxide trimethyl chlorosilane, acetyl chloride or acetyl bromide in glacial acetic acid generated a homogeneous solution. Addition of cyclohexene produced trans-2-halocylclohexyl tellurium trihalides of excellent purity in 70% yield with dichloromethane or ethanol free chloroform. The same compounds hence obtained from heterogeneous reaction mixture, trans 2-methoxycyclohexyl tellurium trich oride was obtained from tellurium dioxide, trimethylchlorosilane and cyclohexene in absolute methanol. In the absence of cyclohexene $TeCl_4$ was obtained in 91% yield from tellurium dioxide and trimetylchlorosilane in $CHCl_3$ and $TeBr_4$ in 98% yield from tellurium dioxide and acetyl bromide in glacial acetic acid[128].

Reactions of aryltellurium (IV), chlorides $ArTeCl_3$ and Ar_3TeCl (Ar = ph, $4-MeOC_6H_4$, $4-HOC_6H_4$, $3-MeO-4-HOC_6H_3$, $2,4-(HO)_2C_6H_3,3,3-bis$ (chloromercurying)-2-4-pentandione and several β diketones and their sodium salts)[129].

The I.R. spectra of twenty four diaryltellurium dicarboxylates are re-

ported. The main bonds in the I.R. are tentatively assigned and their frequency values compared to those data of related compounds. The trigonal bipyramidal arrangement is proposed as the more likely structure for these ocmpounds[130].

NMR chemical shifts, dipole moments and pka values were determined for $RC_6H_4TeX_2C_6H_4NMe_2$-4 (R = 4-Me_2N, 4-MeO, 4-EtO, 4-PhO, 4-Me, H, 4-H, 4-Br, 3-Br, X = Cl, Br, I). The pka values were correlated with substitution constant for $RC_6H_4TeX_2C_6H_4NMe_2$-4 (X = Cl, Br), electronic effects were transmitted more poorly through $TeCl_2$ and $TeBr_2$ groups than through Te by factors of 2.31 and 3.10 respectively. Transmission factors were also observed for the $C_6H_4TeCl_2$ and $C_6H_4TeBr_2$ group.[131]

Comparison of calculated and experimental dipole moments of $(RC_6H_4)_2Te_2$ (R = H, 4-Me, 4-MeO, 4-EtO, 4-Cl, 4-Br, 3-Cl, 3-Br) indicated that in benzene $(RC_6H_4)_2Te_2$ exist tin the gauch form with dihedral angle of 75^u. The effect of including d orbitals of Te in the calculations of the total energy of ditellurides was reported. Rotational barrier for $MeX_2Me(X = S,Se, Te)$ were calculated by the extended Huckel method. The most stable conformation of MeX_2Me was very similar to that of $(RC_6H_4)_2Te_2$[132].

Diphenylene tellurium (IV) dichloride was prepared and its interaction with various silver salts (Ag^+X^-) donor bases (L) and R_4NCl have been studied. Its reduction products dephenylene te (II) undergoes oxidative addition with halogens and interhalogen. It also acts as a Lewis base forming molecular adducts with strong acceptors such as $HgCl_2$. A few organic tellurium derivatives

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show appreciable antiviral activity[133].

$(PhCH_2)_2TeX_2$ (X = iodo, cyano, thiocyanato, IO_3, NO_3 , pyridine, morpholine, piperidine) were prepared and characterized. These compounds are finally or fairly stable. The antibacterial activity indicated that compounds with Te (II) oxidation state possess antibacterial activity comparable to that of tetracycline those of Te(IV) are inactive[134].

$RTeCl_3$ (R = Ph, $4\text{-}MeOC_6H_4$, $6\text{-}PhOC_6H_4$) reacted with $Me_3SiNR^1R^2[R^1 = R^2 = Et, R^1R^2 = (CH_2)_4]$ under dry nitrogen atmosphere to give $(R^1R^2N)TeCl_2$ and Me_3SiCl. The products decomposed to give $(R^1R^2NH_2)^-(RTeCl_4)^-$. R_2TeCl_2 did not react with $Me_3SiR^1R^2$ even on refluxing for 6 hours. R_2TeCl_2 was reduced by Et_2NLi to give R_2Te[135].

Coordinative interaction between $TeCl_4$ or $RTeCl_3$ (R = aryl) and transition metal chelates of the general formula: $R_nTeCl_{4-n}M$ (n = 0 or 1) [(R = Ph, $p\text{-}MeOC_6H_4$, $EtOC_6H_4$,) (M = Ni(II))] LH_2 = Schiff-bases derived form salicyldehyde or ohyudroxy acetophenone on the complexes in solid state indicate coordination of the metal chelates to Te (IV) via 2-phenolic O atoms, planarity about the transition metal ions is thus retaind[136].

$Te(CH_2CH_2Ph)_2$ was prepared by alkylation of Na_2Te with the corresponding alkyl bromide. The resulting slightly air sensitive which can be converted to a stable diiodide and forms stable coordination complexes with $PdCl_2$ and $PtCl_2$. The geometry of these complexes $MCl_2[Te(CH_2Ch_2Ph)_2]_2$ (M=Pd,

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Pt) were studied by far I.R and Raman spectroscopy. The Pt complexes was also studied by[125] Te NMR spectroscopy, a useful probe for observing cistrans isomerization in such complexes and the first Te-Metal coupling constant for such complexes are reported (JTe^{125}-Pt^{195} cis 900 HZ trans 544 HZ)[137].

Treating ph_2TeO with strong lewis acid $SnCl_4$, $TiCl_4$ and $SbCl_5$ gave 75-80% Ph_2TeCl_2 whereas $RTeCl_3$ (R=Me, p- $MeOC_6H_4$, p-$PhOC_6H_4$) gave $RTeCl_3$, Ph_2TeO. The I.R. spectra of (p-$R^1 C_6H_4)_2$ TeO (R^1=H, MeO) Were studied[138].

Some aryl tellurium (IV) compounds (e.g., p-$MeOC_6H_4TeCl_3$) react with iodine and bromine to give the corresponding aryl halides (e.g., p-$MeOC_6H_4I$) in good to moderate yields (iodo and bromoditelluration). The addition of NH_4F, CsF, KF, $SbCl_5$ and $HgCl_2$ accelerates the reacion in some cases compared to these haloditellurium, chloroditelluration and cyanoditelluraion of these compounds were very sluggish[139].

Twenty five p- $RC_6H_4TeCl_3L$ (R = MeO, PhO; L = N-, O- and S-donor Lewis bases e.g., Et_2N, Ph_3PO, Me_2SO) were prepared by treating $RTeCl_3$ with L in CH_2Cl. They were screened for their antibacterial and antifungal activities [140].

Reaction of Ph_2TeCl_2 on p-$EtOC_6H_4TeCl_3$ with donor ligands for example, pyridine, DMF, Me_2So_3, Ph_3ps etc. gave 1:1 complexes. A few of the complexes showed activity against gram negative bacteria. All of the com-

pounds were completely inactive towards pathogenic fungi[141].

RTeCl$_3$ (R = 4-MeOC$_6$H$_4$), 4-HOC$_6$H$_4$) reacted with (R$^1_4$N)X(R^1 = Me,Et,Ph,Bu X = Cl, Br,I) to give (R$^1_4$N(RTeCl$_3$X))(X = SCN, iodo) were also prepared. The fungicidal and bactericidal activity of RTeCl$_3$ was affected by complexation[142].

Treatment of mercaptan to azines with Te(IV) halides in dioxanes THF or Me$_2$CHOH gave 2:1 adducts configuration, the thione tauutomer of the heterocycles, e.g. treatment of 1-methyl-2 imidazolethiol with Tecl$_4$ in dioxane gave 93% of the 2;1 adduct (TeCl$_4$L$_2$) dioxane (L = 1-methylimidazole-2(3H)thione). The Te (IV) ion in the adducts has a sterically inert lone pair and thus a pseudooctahedral coordinations[143].

Condensation of TeF$_4$ or TeCl$_4$ with Me$_3$SiNR$_2$ (NR$_2$ = Et$_2$N, morpholine, piperidine) in C$_6$H$_4$ gave 46-94% (R$_2$N)$_2$ TeX$_2$ (X = F,Cl). Treatment of (R$_2$N)$_2$TeF$_2$ (R$_2$N = morpholine) with (Me$_3$S)$_2$NSO$_3$C$_6$H$_4$P^1-4 (P^1 = H,Me) gave (R$_2$N)$_2$TeNSO$_2$C$_6$H$_4$R^1-4[144].

RC$_6$H$_4$TeCl$_3$ (R = 4-Me, H, 4-MeO, 4-EtO, 4-PhO, 4-Cl, 4-Br, 3-Cl, 3-Br, 3-O$_2$N reacted with 4-AcOHgC$_6$H$_4$NMe$_2$ in refluxing dioxane to give RC$_6$H$_4$Te Cl$_2$C$_6$H$_4$-NMe$_2$-4. The dipole moments increased in the state order R and their basicity constants decrease in approximate, the same order A correlation analysis indicated transmission coefficient of 0.16 and 0.54 for the C$_6$H$_4$Te

and Te bridging groups respectively[145].

Ph$_2$Te(O$_2$CCF$_3$)$_2$ forms 1:1molecular adducts with various N,O and S donor basis. The corresponding reactions with Ph$_2$Te (O$_2$CCCl$_3$)$_2$ depend upon the nature of the bases. Ph$_2$Te (O$_2$CCCl$_3$)$_2$ give 1:1 molecular adducts with diethyl acetamide and morpholine (whereas the 4picoline, tetramethyl piperidine and dimethyl acetamide ligands L afford (Ph$_2$TeCl$_2$L with 3-picoline-M-oxide (L^1) and Cl$^-$ and (Ph$_2$Te (CCl$_3$)$_2$L^1) and (Ph$_2$Te (CCl$_3$)$_2$Cl)$^-$ respectively are obtained[146].

The reaction of bis (benzoyl) tellurides with primary or secondary amines or potassium ethanoiate yield the corresponding tellurobenzoic acid salts, which are readily oxidized with iodine or benzene sulfonylurea chloride is afford novel bis (benzoyl) ditelluride[147].

Treating 3-(RC$_6$H$_4$OSiMe$_3$ (R=H, Me) with TeCl$_4$ in PhMe gave 82-89% below Fig.24 compounds. Bromosalicyldehyde derivative Fig.24 (b) gavetrichlorotellurium derivative Fig.24(c), which is stabilized by carbonyl O-Te interaction[148].
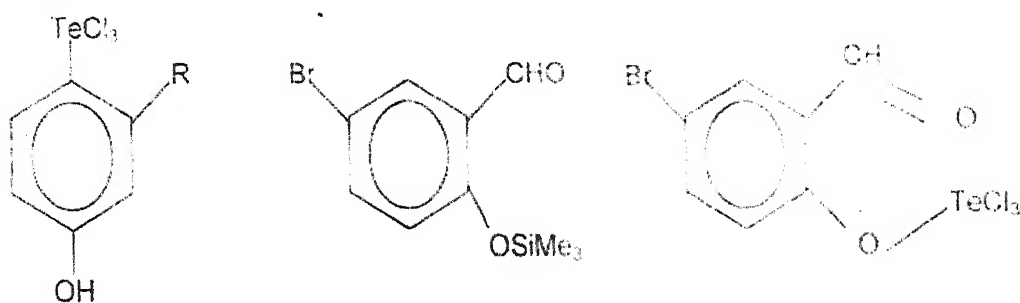
Fig. 24

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$(R_4N)_2 [Ph_2Te(NO_3)_2X_2]^{2-}$ (R = Me, Et, Bu; X = Cl, Br, I, NO_3) were prepared and characterized, physicochemical studies suggested are octahedral geometry for the anions[149].

The pentacoordinated Te(IV) complexes $[R_2TeCl_2.L]$(R = C_6H_5, p-$CH_3OC_6H_4$; L = Ph_3PSe; (p-$MeC_6H_4)_2pSe$, (Ph_2P-(Se)$(CH_2)_2SePh_2$) were prepared by the reaction of R_2TeCl_2 with L under anhydrous condition. The reaction of $RTeCl_3$ and L, however yields tellurium/selenium metal $^1J(31P-^{77}Se)$ coupling constant data suggest complexation. In case of bidentate donor bases only one donor site is used in coordination. The complexes posses distorted octahedral geometry around a central Te atom which is surrounded by five groups and one vacant site occupied by a lone pair[150].

Thermal analysis indicated that 4-$RC_6H_4TePhX_2$ (R = H, Me, X = Cl) form 1:1 complexes with SbCl5. In 1:3 complexes two of the $SbCl_3$molecules occupy equivalent positions (R = H, X = 1) forms only 1:3 complex with $SbCl_5$[151].

Me_3SiO(Ph = CH_2) reacted with $TeCl_4$ in Et_2O and with $RTeCl_3$ (R = 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, (4-$EtOC_6H_4$) in C_6H_4 to give 63% $(PhCOCH_2)_2$ $TeCl_2$ and 87-91% $PhCOPh_2TeCl_2$ respectivity[152].

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(p- $RC_6H_4)_2TeCl_2$ (R = H, Br, Me, MeO) were prepared in 86-87% yields by refluxing (p- $RC_6H_4)_2Hg$ with $TeCl_4$ in dioxane one hour, p-$MeOC_6H_4TeCl_2C_6H_4R$-p (R = H, Me) were prepared in 93-97% yields respectively refluxing p-$MeOC_6H_4Tecl_3$ with (p- $RC_6H_4^1)_2Hg$ dioxane 8 hours[153].

The reaction of $(CF_3)_2TeF_2$ with BF_3, AsF_5 and SbF_5 yield the new complex compounds $[(CF_3)_2Te][B_{F4}]$ and $[(CF_3)_2TeE][CF_6]$ (E = Sb, As) whereas the reaction of $(CF_3)_2TeX_2$ (X = Cl, Br) with halide acceptors caused only decomposition $(CF_3)_2TeX_2$ form with MX (X = F, Cl; M=K, Cs, Ag) isolable salts $M[(CF_3)_2TeX_3]$, $M[(CF_3)_2TeBr_3]$ is only detected in solution evidence for the formation of hexa coordinated tellurates(IV) $M_2[(CF_3)_2TeX_4]$ is found[154].

The interaction of organotellurium trichlorides, p- $RC_6H_4TeCl_3$ (R = H, OH, OCH_3, OC_2H_5) with Lewis bases (quinoline, 1-methyl-2-pyrolidinone, tetramethylene sulfoxide or 2-aminothiozole) led to the isolation of 16 Lithertato unknown stable molecular adducts. They were screened for their gridae properties and found to be more active against bacteria than fungi[155].

Diphenacyltelluriumdihalides, dipseudohalide, dioximes, dithiacarbamate derivatives e.g. $PhCOCH_2TeR_2$, CH_2COPh (R = iodo) Br, NCS, CN, S_2CNHPh, piperidinodithiacarbamate and adducts with some nitrogen donors, e.g., $PhCOCH_2TeR_2(Br_2)CH_2COPh$ (R^1_2 = pyrralidine, pyridino, piperidino,morpholine) have been synthesized and characterized. The

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tetracoordinated organotellurium compounds exhibit keto-enol tautomerism with end form being present to the extent of ~50% while the hexacoordinated Te adducts exist in the keto form. The proton of the enlol form and hydroxy proton of oximes derivative are attached to the lone pairs of Te atoms forming Te-H bonds[156].

$[HO(CH_2)_2]_2NCS_2H(LH)$ prepared in solution by mixing $[HO(CH_2)_2]NH$ with CS_2 reacted with Se and Te compounds to give TeL_4, TeI_2L_2, $TeIL_3$, TeL_2 and SeL_2. The complexes were characterized by analytical,IR and electronic spectra and thermogravimetric analysis[157].

A freshly prepared solution of tellurocyclopentane diperchlorate reacts with Lewis bases to yield cation complexes $[RTeL_2](ClO_4)_2$ (R = cyclopentyl, L = pyridine-N-oxide lutidine, N-Oxide, β-picoline-N-oxide, quinoline-N-oxide, 2,2-bipyridyl). All were characterized and proposed to have a trigonal bipyramidal structure with one lone pair of electrons occupying on the positions[158].

R_2TeL_2 (R = Ph or $p - MeOC_6H_4$) have beeen prepared by the reaction of R_2TeCl_2 with NH_4L in anhydrous toluene. The product have been characterized using analysis and spectroscopic IR, ^1H, ^{13}C, ^{125}Te NMR data. The products are monomeric in nature and their possible structures are reported[159].

Several new dimethyl tellurium dicarboxylates $Me_2Te(OCOR)_2$ (R = alkyl,

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aryl) were prepard in high yield and characterized. A probable nonionic trigonal bipyramidal structure was deducted from spectroscopic and conductance data[160].

Organotellurium compounds $(Ph_2CH_2CH_2)_2TeRX$ (R = Br, Cl, cyano,iodo,Me, Et,CH_2CHCH_2Ph; X = Br,Cl, I) were prepared and characterised $(PhCH_2CH_2)TeRX$ (R = alkyl,sameX). Readily eliminated Te alkyl halide in DMSO conductivity measurements indicated that thetellurides behave as weak electrolyte[161].

Diaryltellurium bis(trihaloacetate) and diarylchlorotellurium trihaloacetates e.g., $(MeOC_6H_4)_2Te(O_2CCF_3)_2$ and $(MeOC_6H_4TeCl(O_2CCF_3)$ have beeen prepared by metathetical reaction between corresponding dichloride and $AgOCOCF_3$ or $NaOCOCl_3$ respectively. A convenient synthesis of diaryltellurium bis(trifluroacetate) from the corresponding telluroxides and trifluroacetic anhydriede is reported. These compounds have been charaterised by IR, ^1H and ^{19}F NMR spectra and X-ray diffraction studies[162].

12-tetracoordinated diorganotellurium(IV) oximates of the type $Ar_2TeCl(ONCRR')$, $Ar_2Te(ONCRR')_2$ [Ar = Ph, p- MeC_6H_4, RR' = Me, Me:Me, Ph:Me, Et:Ph, Ph:$(CH_2)_5$] have been synthesized either by the reactions of diorganotellurium (IV) dichlorides with appropriate oxime in the presense of Et_3N or by the metathetical reactions of Ar_2TeCl_2 with the corresponding sodium salt of the ligand. The organotellurium(IV) oximate derivatives have

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been characterised by elemental analysis, IR, NMR, molecular weight and conductance data[163].

Organotellurium oximates R_2TeL_2 ($R_2 = Me_2$,(p-$MeOC_6H_4)_2$, diphenylene L=8-hydroxyquinolinate,8-hydroxy-2-ethylquinolinate have been prepared in quantitative yields by the interaction of R_2TeX_2 (X = Cl,Br,I) with NaL or HL. R_2TeL_2 react with R^1CO_2H(R^1 = CF_3, CCl_3, $CHCl_2$, CH_2Cl) to yield mixed ligand complexes $R_2Te(OCOR')L$. The proton magnetic and I.R. spectra suggest that R_2TeL_2 possess two types of oxime groups, one of which is bidentate and the other unidentate. The Te atom thus prefers to remain pentacoordinate in an octahedral geometry, one of the sites being occupied by a lone pair[164].

Hydrolysis of bis(hydroxyaryl)tellurium dihalide appears to in a stepwise manner. In neutral medium $R_2Te(OH)X$(X = halide ion, R = 4-hydroxy phenyl, 3-methyl, 4-hydroxy phenyl) have been lisolated. Further, hydrolysis does not occur appreciably. Alkaline hydrolysis (with NaOH) yield $R_2Te(OH)_2$ which on heating at 100^0c changes to R_2TeO. Isolation of the intermediates in this case is not possible but they are indicated by Ph metric and conductometric titrations. Hydrolysis of these compounds, follows the order Cl>Br>I and O-cresol>phenol[165].

Te reacted with RCl (R = acetyl) to give R_2Te, which react with SO_2Cl_2 or $Pb(OAC)_4$ to form R_2TeCl_2 or $R_2Te(OAc)_2$ or R_2Ph_2TeO with maleic anhydride gave $[R'_2Te(ma\ eate)_2]$(R^1 = acetyl, Ph) which were dimeric. Dimeric

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$[R_2^2Te(SCH_2CH_2CO_2)_2]$ (R^2 = Ph, 4-MeOC$_6$H$_4$) were prepared from R$_2$TeO and HSCH$_2$CH$_2$COOH.R$_2^2$TeO (R^2 = 4EtOC$_6$H$_4$) reacted with HSCH$_2$COO(CH$_2$OC$_6$H$_3$(6H)Bu-3,4-(HSR^3)) to give monomeric $R^2Te(SR^3)_2$.

Telluracyclopentane (R^4 = iodo) or Ph$_2$TeCl$_2$ and AgO$_2$CKH:CHCOOBu gave monomeric [R^4 = (OOCCH:CHCOO)-Bu] or Ph$_2$Te(O$_2$CCH:CHCO$_2$Bu)$_2$ respectively. Attempte to preparation of hexyl or octyl Te compounds from Te and R^{5}Br(R^5 = hexyl, acetyl) in presence of Et$_4$N$^-$Br$^-$ gave Et$_4$N$^-$Te$^-$Br$_3$ which was brominated to from Et$_4$N$^+$Te$^-$Br$_5$[166].

Reaction of (p-RC$_6$H$_4$)$_2$Te(O$_2$CR^1)$_2$ with R^{1}COCl (1:2) in CHCl$_3$ or CCl$_4$ gave (p-RC$_6$H$_4$)TeCl$_2$ and (R^{1}CO)$_2$O (R = H, MeO, R^1 = Me,Ph, Et)[167].

The reaction of (p-RC$_6$H$_4$)$_2$TeO with (R^{1}CO)$_2$O gave sixteen (p-C$_6$H$_4$)$_2$Te(O$_2$CR^1)$_2$ (R = H, Me, OMe, NMe$_2$; R^1 = Me, Ph, ClCH$_2$, F$_3$C). Similarly, (p-RC$_6$H$_4$)$_2$TeO and RCOOH gave (p-MeO-RC$_6$H$_4$)Te(O$_2$CR)$_2$ (R = Me,CCl$_3$). The reaction of (p-C$_6$H$_4$)$_2$TeO with HX gave [(p-RC$_6$H$_4$)$_2$Te$^-$OX]X$^-$ (R = H, OMe; X = ClO$_4$, O$_2$CCCl$_3$). Also (p-RC$_6$H$_4$)$_2$Te(O$_2$CR^1)$_2$ and R^{1}COCI gave (p-C$_6$H$_4$)$_2$TeCl$_2$Me, MeO)[168].

The compounds (4-RC$_6$H$_4$)$_2$Te(O$_2$CR^1)$_2$ (R = H, MeO, R^1 = CF$_3$, CCl$_3$, CHCl$_2$, CH$_2$Cl) and Me$_2$Te(O$_2$CCF$_3$) were prepared and characterised. Thus Ph$_2$TeCl$_2$ was treated with CF$_3$COOH and Ag$_2$O in CH$_2$Cl$_2$ to give>70% (R = H, R^1 = CF$_3$). The IR spectral data of the compounds indicates that both

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haloacetate groups are equivalent. In refluxing PhMe the trichloroacetates undergo decarboxylation followed by elimination of diclorocarbene and yielding diorganotellurium dichlorides[169].

TeL_2X_2 (L = thiooxime, X = I, Br) and TeL_3X (X = Cl, Br, I) were prepared from Te(IV) solution contained ML and KX. The complexes were characterized by I.R.[170].

$(p-RC_6H_4)_2TeO$ (R = H, Me, MeO,Me$_2$N)reacted with HCOOH in Me_2CHOH at 60°c to give 61-90% $(p-RC_6H_4)_2Te(O_2CH)_2$(same R) which decomposed in refluxing o-xylene to give quant yields of $(p-RC_6H_4)_2$(same R) and HCOOH[171].

. $RR'Te(O_2CR)_2$ (R = $p-MeOC_6H_4$, $p-EtOC_6H_4$, R' = $PhCH_2COPh$, $CH_2COMeC_6H_4NMe_2-p$, R^2 = Me, CH_2, Cl, Ph) prepared by the metathetical reaction of Ag carboxylates and organotellurium dichlorides act as a unidentate ligands. The thermogravimetric curves for $[p-MeOC_6H_4Te(C_6H_4NMe_2)-p](CO_2CR^2)_2$ (R^2 = Me, Ph) indicates decomposition at 240°-260°C with loss of 2 moles of CO_2 giving unstable telluraorganotellurium which further decomposed at 380°-400°C yielding R_2^2 Te. All these compound prepared were antibacterial[172].

The compounds R_2TeXY [R = hydroxyaryl, HOC_6H_4, $1,2-(HO)_2-C_6H_3$, $1,3-(HO)_2C_6H_3$, X,Y = halo,OH] particularly diaryl tellurium hydroxides are prepared in one step process with high yield ~95%, by reaction of R_2TeAB (A,B = halo, OH) with an alkali metal hydroxides. R_2TeXY are useful in precursor of semiconductors. A mixture of $(4-HOC_6H_4)_2TeCl_2$ and aqueous NaOH was heated at 400C for 10min., to give R_2TeXY (R = $4-HOC_6H_4$; X=Y=OH)[173].

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Solutions of diorganotellurium (IV) diperchlorates R_2Te $(ClO_4)_2$ (R = Ph, p-MeOC$_6$H$_4$); may be prepared by the reaction of R_2TeCl_2 and $AgClO_4$ on by the reaction of diorganotelluroxide with excess of 70% $HClO_4$. I.R. and conductivity data indicates that Ph_2Te $(ClO_4)_2$ possesses a covalently bonded perchlorates groups in solution. Interaction of the freshy prepared solutions with Lewis bases affords cationic complexes of the types$[R_2Te(ClO_4)(L)][ClO_4]$ and $[R_2Te(L_2][ClO_4]_2$ which have been characterized by I.R., elemental analyses and conductivity measurements. The DMSO complex is as (Fig.25).
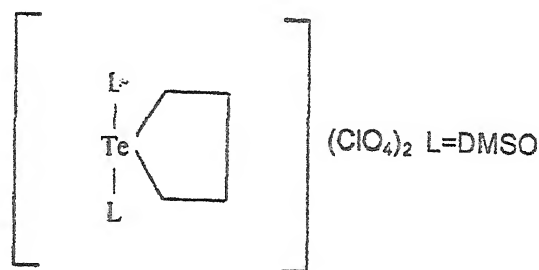
Fig. 25

Explodes at its melting points174.

$Ph_3TeXTiX_4$ and $2Ph_3TeX.TiX_4$ (X = Cl,Br) are obtained by reactions of Ph_3TeCl and Ph_3TeBr with TiX_4. Ph_3TeI and TiI_4 yield only Ph_3TeI, TiI_4. Conductivity and molecular weight determination are consistent with their dissociation in dilute solution as Ph_3Te^+ and TiX_5^- or $PhTe^+$ and TiX_6^{2-} units. Far IR spectra reflect the formation of TiX_5^- and TiX_6^{2-} for 1:1 and 2:1 adducts respectively. The formulation of these compounds are given as$[Ph_3Te]^-[TiX_5]^-$

and $[Ph_3Te]_2^+ [TiX_6]^{2-175}$.

$Ph_3TeX.SnCl_4$ and $2Ph_3TeX.SnCl_4$ (X = Cl, Br, I) are obtained by reactions for Ph_3TeX with $SnCl_4$. Conductance , molecular weight determination and ^1H NMR data are consistent with disscociation of adducts in dilute solution Ph_3Te and $SnCl_4X^-$ or Ph_3Te^- and $SnCl_4X_2^{2-}$ units. The absence of Te-Sn and Te-X vibration in the far IR of these copounds reflect the transfer of X from Ph_3TeX to $SnCl_4$. The formulation of these adducts are proposed as $[Ph_3Te][SnCl_5][\ Ph_3Te]_2[SnCl_6]$, $[Ph_3Te][\ SnCl_4Br]$, $[Ph_3Te]_2[SnCl_4Br_2]$, $[Ph_3Te][\ SnCl_4]$ and $[Ph_3Te][\ SnCl_4I_2]^{176}$.

The first synthesis of tetratelluradicyclopentanampntalen which is six membered ring isomer of hexamethylene tetratellurafulvalene from 1,2-dibromocyclopentene and $Cl_2C=CCl_2$ is reported. It was obtained as yellow microcrystals[177].

Fig. 26

(52)
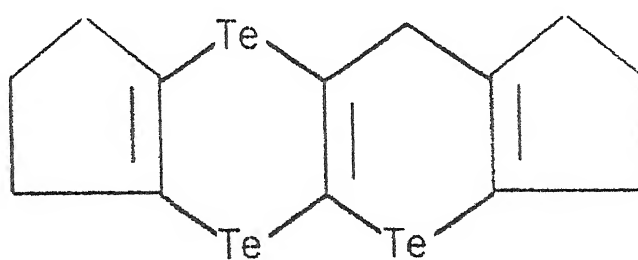
Diaryl tellurides RTeR'R = R' = Ph, p-MeOC$_6$H$_4$; R=Ph, R' = p-MeOC$_6$H$_4$) react with allyl bromide cyclohexyl iodide. MeIPhX (X = Br,I) or SnI$_4$ to give corresponding triorganotellurium halides.the Te-allyl bond is readily cleaved by electrophiles such as Br$_2$, I$_2$, ICl,' BrCN, ICN. Thus Ph$_2$Te (CH$_2$CH:CH$_2$)Br, which with I$_2$, IBr and BrCN gave 62-85% Ph$_2$TeIBr, Ph$_2$TeBr$_2$ and Ph$_2$TeBrCN respectively[178].

Reaction of Tecl$_4$ with o-or-m-ClC$_6$H$_4$OH gave 3,4-Cl(OH) C$_6$H$_3$TeCl$_3$ and 2,4-Cl(OH)C$_6$H$_3$TeCl$_3$ respectively which on halogen exchange with KBr and KI gave the corresponding TeBr$_3$ and TeI$_3$. Conductance and cryoscopic measurements show that the TeCl$_3$ are almost nonionic, whereas the TeBr$_3$ and TeI$_3$ re 1:1 electrolytes in PhNO$_2$, Me$_2$SO and MeCN. The ^{1}H NMR spectra indicate that the TeX$_3$(X = halo) groups are para to the OH group. The far I.R. spectra reflect the polymeric mature of these compounds[179].

Cresyltelluriumchloride were prepared treating cresols with TeCl$_4$. Other halides were obtained by halogen exchange of the chlorides with KBr or KI. Conductivity and cryoscopic measurements indicates that RTecl$_3$ (R = cresyl) and R$_2$TeX$_2$, (X = halogen) are molecular compounds. While RTeBr$_3$, RTeI$_3$ and R$_3$TeI are ionic compounds[180].

(4-HOC$_6$H$_4$)nTeX$_{4-n}$(n= 1 or 2, X = Br, Cl or I) and (1,2 and 1,3 (OH)$_2$C$_6$H$_3$)nTeX$_{4n}$(n = 1,2 or 3; X = Cl, Br or I) were prepared. The chlorides by direct reaction of the hydroxyl benzene with TeCl$_4$ in CHCl$_3$, the bromides

and iodides by halogen exchange of the chloride. The conductivity and cryoscopic measurement shows that materials of the type $RTeBr_3$ and $RTeI_3$ and R_3TeX (X = Cl, Br, I) behaves as 1:1 electrolytes in dilute solutions, whereas compounds with comparisons, R_2TeX_2 exhibits molecular properties and to polymerize at higher concentration[181].

$[R_2Te(O-O-C_6H_4(R^1NR^2N:CR^1-C_6H_4O-O)]$ $(R^2 =(CH_2)_4$, R = Ph_2, p-$MeOC_6H_4$, p-$EtOC_6H_4$, R^1 = M, R^2 = C_2H_4, R = Ph, R^1 = CH_3, R^2 = CH_2CH_2, R = Ph, R^1 = H, R^2 = $O-C_6H_4$ and $[Ph_2Te(O-OC_6H_4CH =:NR^3X)][R^3$ = $O-C_6H_4][X = O,S, R^3 = C_6H_4$, X = O] were prepared and characterized by elemental analysis, electrical conductivity, molecular weight, IR and H^1 NMR measurement. The complexes are monomeric and non electrolytes in $PhNO_2$ [182].

R_2TeCl_2 (R = Me, Et) reacted in HCl SO_3 to give 40-60% $R_2Te(SO_2Cl)_2$. Electrical conductivity showed to be nonionic and IR spectroscopy gave a reduced Cs symmetry for the SO_3Cl which indicates covalent bonding in it[183].

Several organotellurium derivatives of the general foumaula $C_8H_8TeX_2$ (x = Cl, Br, I, SCN, $OCOCH_3$, $OCOCH_2Cl$, OCOPh), $(R_4N)^-$ $(C_8H_8TeI_2X^-)$ (R = Me, Et, Bu; X=Cl, Br) and RR^1TeX_2 (R = p-$MeOC_6H_4$, R = $C_6H_4N(CH_3)_2$; X = Cl, $OCOCH_3$, OCOPh were tested against five bacteria (Bascellus subtilis, staphylo cocus) aureus, Escherechia coli, Salmonella typhi, Mycobacterium tuberculosis, and one fungus (Aspergillus terrus).

The antifungal activity of the anionic complexes was higher than their antibacterial activity compared to the parent compound $C_8H_8TeI_2$[184].

$RC_6H_4TeX_2C_6H_4R^1$ (R = H 4-F, 4-MeO) R = H, Me, MeO,X = Cl,Br) were prepared it. 60-90% yields by treating $(RC_6H_4)_2Te_2$ with $R^1C_6H_4N_2^-$ in the presence of $CuCl_2$ or $CuBr_2$[185].

The reaction of $(C_2F_5)_2Te$ and XeF_2 in SO_2ClF yielded $(C_2F_5)_2TeF_2$ essentially quantity chlorine and $(C_2F_5)_2Te$ gave $(C_2F_5)_2TeCl_2$. Both $(C_2F_5)_2TeF_2$ and $(C_2F_5)_2Te\ Cl_2$ were assigned a trigonal bipyramidal geometry on the basis of their ^{19}F NMR and vibrational spectra with the lone pair and C_2F_5 groups in equatorial and the halogens in the axial positions. $C_2F_5TeF_3$ was prepared, essentially quantity by the reaction of $C_2F_5Te.TeC_2H_5$ and XeF_2 in liquid SO_2F_2. Generally inert SO_2ClF was found to react with $C_2F_5TeTeC_2F_5$ to give C_2F_5TeCl XF_{3-X} and SO_2. T he structure of $C_2F_5TeF_3$ was determined by X-ray diffraction. Each tellurium atom is surrounded by two terminal fluorine atoms and two bridging fluorine atoms and a C_2F_5 group in an axial position around the apex fo distorted square pyramidal. The square pyramidal units are linked by symmertrical bridging atoms into endless chains with bridging angles of 180^0 and 177^0. The geometry of the $(C_2F_5TeF_4)$ group is consistent with steric activity of the nonbonded electron pair. The ^{19}F NMR and Raman Spectra of $C_2F_5TeF_3$ were recorded and the Raman spectrum assigned trans $C_2F_5TeClF_5$ was prepared by the reaction of $C_2F_5TeTeC_2F_5$ and an excess of ClF. The trans octahedral geometry of $C_2F_5TeClF_4$ was unambiguously assigned from its ^{19}F NMR and vibrational spectra.A mixture of trans $(C_2H_5)TeF_4$ and trans

(55)

$C_2F_5TeCl_4$ was obtained from the reaction of $(C_2F_5)_2$ Te and and excess of CIF trans geometry of $(C_2F_5)_2TeF_4$ was unambiguously assigned from its ^{19}F NMR spectum[186].

The sensitivity and reactivity of some new α, α' – bis(2 and 4 substituted benzoyl) $TeCl_2$ (R = H, NO_2, CH_2Cl_2, CONH etc. R^1 = H, NO_2, OMe etc.) Fig.27 are reported. Te-C bond remains stable in many interesting inter conversions of these derivatives 2-substituted derivatives were intramolecular coordinated with the central metal atom [187].
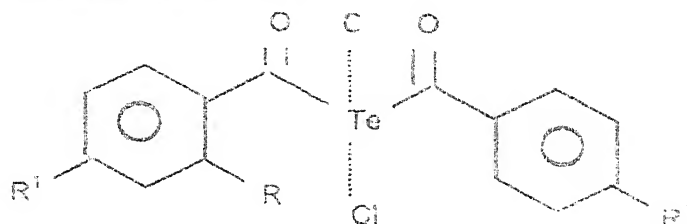
Fig. 27

Electrophilic substitution of Fig.28(a) (R = H) with $TeCl_4$, 4hrs refluxing C_6H_6 gave 85% Fig.28(a) (R = Cl_3Te) which was heated in an oil bath 1.5hours at 190^0-200^0C to give hydrochloride fig.28(b) The letter was dechlorinated with $Na_2S_2O_7$ followed by neutralization to yield naphthaledene Fig.28(c)[188].

(a)

(b)

(c)

Fig. 28

(56)
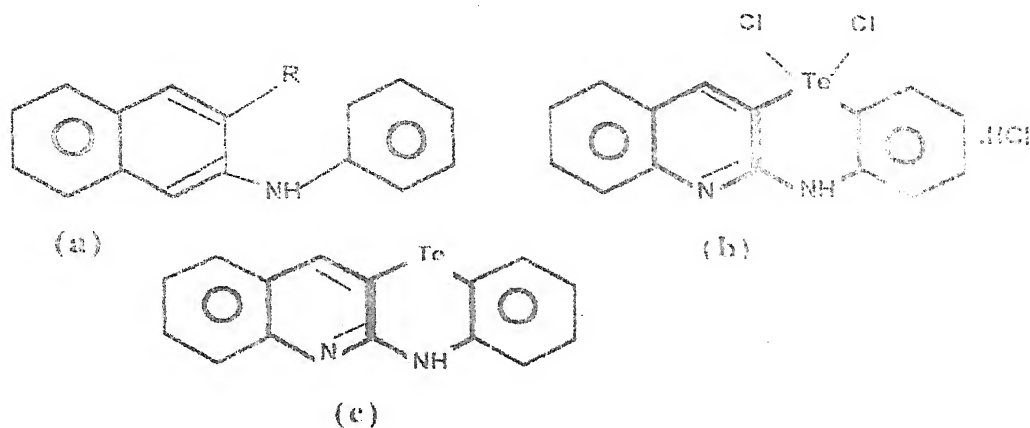
Trans metalation of RHgCl (R = 2-(2-pyridyl)phenyl-2-(quinoline-2-yl)phenyl with TeBr$_4$ gave organotellurium tribromides RTeBr$_3$. Reduction of the tribromides gave RTeBr and dimmers R(Te)n R(n = 1-3))[189].

The reaction of Bu$_4$N[TeF$_5$] with HOCHCH$_2$NH$_2$-1-amino -2 propanol, 2-aminobutanol and 3-amino-1-propanol was followed by ^{19}F and [125]Te NMR. The all cases TeO$_3$L (L = Amino alcohol) were formed in which there are 3Te-F hypervalent bonds[190].

The reaction of unsaturated alcoholwith aryl tellurium trihalides gave cyclic ethers bearing an aryl dihalotelluro group in β-position.
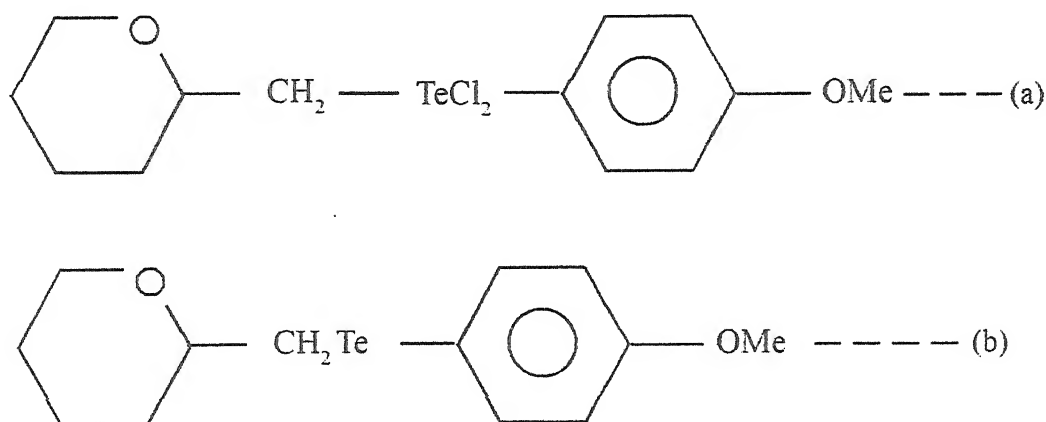
Fig. 29

Reduction of the Te-Cl bond with thiourea dioxide gave the Tellurides. Thus the reaction of CH$_2$-CH(CH$_2$)OH with 4-MeOC$_6$H$_4$TeCl$_3$ gave 90% yield of dihalotelluro ether Fig.29(a) which on reduction gave 93% yield of telluride Fig29(b)[191].

(57)

The compounds $R_2Te[(O)N = CMeC(NOH)Me]_2$ (R = ph, anisyl, Me) were prepared when Ph_2TeO was treated with $MeC(=NOH)C(=NOH)Me$ (when R = Ph)[192].

$(PhCOCH_2)_2TeX_2$ (X = Br, iodo, SCN) S_2CNR_2 (NR_2 = anilino, piperidino) and $(PhCOCH_2)_2TeBr_2(NR^1_3)_2$ (NR^1_3 = amines) were prepared. Spectral studies indicated that the tetracoordinated tellurium compounds $(PhCOCH_2)_2TeX_2$ exhibited keto-enol tautomerism (enol form to the extent of 60%). The hexa coordinated Te compounds $(PhCOCH_2)_2TeBr_2(NR^1_3)_2$ [193].

The reactions of $\alpha\text{-}Me_2TeI_2$ with $M_2(CO)_{10}$ (M = Mn, Re) $CO_2(CO)_8$, $Na(Co(CO)_4$ and $Na(Mn[CO]_5]$ gave $cisM(CO)_4 Te(Me_2)I$, $[CO(CO)_5 TeMe_2]_2$, $[Co(CO)_4]_2TeMe_2$ and $Mn(CO_5)_2TeMe_2$ respectively (Cp $Mo(CO)_3)_2$ (Cp = cyclopentadienyl) did not react with $\alpha\text{-}Me_2TeI_2$ whereas $(MeCp)MN(CO)_3$ (MeCp = methyl cyclopentadienyl) gave a brown oil. The complexes were characterized by I.R. spectra[194].

(a)   (b)
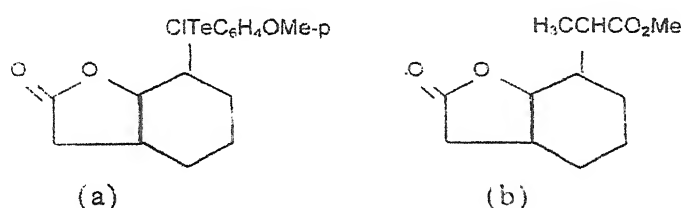
Fig. 30

The lactones fig.30(a) and cyclic ethers produced in the tellurocyclo functionalisations of unsaturated carboxylic acids and alcohol are efficiently detallurated with $CH_2=CHCO_2Me$ leads to the corresponding adducts Fig.30(b) in moderate to good yield[195].

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1-(NMe$_2$)-4-MeC$_6$H$_4$ on o-mercuration followed by reaction with ArTeCl$_3$ (Ar = Ph, 4-MeOC$_6$H$_4$ or 4-EtOC$_6$H$_4$) gives 1-(NMe$_2$)-2-(Ar-TeCl$_2$-4-Me-C$_6$H$_3$) which on reduction with Na$_2$S$_2$O$_5$ gives 1-Me-3-N-2-TeAr-4-Me.C$_6$H$_3$(L).L were characterized by elemental and typical reaction with MeI, IR, ^{1}H, ^{13}C NMR spectra, molecular weight and conductance measurements. L reacts with Na$_2$MCl$_4$/K$_2$MCl$_4$ (M = Pt or Pd) resulting the MCl$_2$.L. These complexes are monomeric nonelectrolytic and diamagnetic indicating square planar arrangements of ligands around the metal which is supported by electronic spectra.^{1}H NMR data in conjunction with IR spectra suggest that L behave as bidentate ligands in these complexes[196].

Lithiation of Ph$_2$CH$_3$NMe$_2$ followed by reaction with Te(S) and air oxidation gives a poorly defined tellurium anhydride. Halogenolysis with Br or SO$_2$Cl$_2$ gives o-Me$_2$NCH$_2$C$_6$H$_4$TeX$_3$ (X = Br, Cl). Lithiation of PhCH$_2$NMe$_2$ followed by reaction with Te(S) then an alkyl halide, then SO$_2$Cl$_2$ give o-R^{1}TeCl$_2$, C$_6$H$_4$CH$_2$NMe$_2$(R = Me, Et, Bu). The structure of o-Me$_2$NCH$_2$C$_6$H$_4$TeX$_3$ (X = Br) and the HCl salt of o-X$_2$TeCl$_2$C$_6$H$_4$CH$_2$NMe$_2$ (X = Br) were determined by X-ray crystallography. The coordeination of Te in both compounds is essentially octahedral with vacant equatorial site[197].

The butyl methyl [2-[(phenylimino)methyl] phenyl tellurium perchlorate compound was prepared in 78% yield by treating 2-BuTeC$_6$H$_4$CH:NPh with MeI in Me$_2$COCl and then
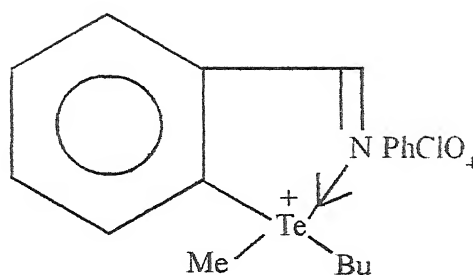
With $AgClO_4$,$3MeCHI$. The structure was determined by X-ray crystal-lography[198].

Me_2TeX_2 (X=Cyano, NCO,N_3) have been synthesized by metathesis of Me_2Te with two equivalent AgX in $CHCl_3$. Reactions of $Me_2Te(N_3)_2$ with Ph_3P and Me^+N^-Cl yields $Me_2Te(N=PPh_3)_2$ and $Me_2N^-Me_2(N_3)_2Cl^-$ respectively [199].

Halogenation of butyl tellurobenzal anilines (R=H,R^1=H,Me,MeO, R=R'=F; R"=Bu) gave halogenotellurobenzalanilines (R^2=Cl,Br,Iodo) and (R^2=Cl,Br, Iodo). The effects of structural feature upon the length of M-Te intramolecualr coordination bonds were studied by X-ray and $^{125}TeNMR$[200].

Reaction of R_2Te_2 (R=Ph, 4-MeC_6H_4) with Na in THF containing HMPA generated tellurolate anions which on treatment with SO_2Cl_2 gave 80% $R(Et)TeCl_2$, which on treatment with $NaOCH_2CF_3$ in CF_3CH_2OH gave 77-78% R(Et) Te $(COOCF_3)_2$ [201].

Cyclohexene or cyclohep.tene reacts with $TeCl_4$ or $TeBr_4$ and an alco-holic in CCl_4 to give the 2-alkoxy-trans-cycloalkyltellurium (IV) trihalides com-

pounds ^{13}C and ^{1}H NMR and mass spectral data were reported [202].

Reaction of p-RC$_6$H$_4$COCl$_2$ (R=MeO,O$_2$N) with Te (S) and NaI gave 52.73% (p-RC$_6$H$_4$CO)$_2$TeI$_2$. Demethylation of (p-RC$_6$H$_4$CO)$_2$ TeI$_2$ (R=O$_2$N) gave (p-RC$_6$H$_4$CO)$_2$TeI$_2$ (R=OH). Underwent acetylation and chloroacetylation without cleavage of the C-Te bond[203].

The reaction of methyl ketones, RCOCH$_3$(R=Ph,4-MeC$_6$H$_4$, 2-thienyl, Me$_3$C) with TeCl$_4$ in CHCl$_3$ gives 29.56% (RCOCH$_2$)TeCl$_2$ which were reduced to the corresponding diketo tellurides (3-tellurapentane-1,5-diones, (RCOCH$_2$Te) by aqueous Na$_2$S$_2$O$_4$. Physical and chemical properties of dike to telluride's are also reported[204].

Iodine monohalides (ICl,Ibr) CNI and (SCN)$_2$ add oxidatively to R$_2$Te (R=Ph, p-CH$_3$OC$_6$H$_4$) under mild condition (~5)^{0}c. The resulting organotellurium(IV) derivatives e.g. Ph$_2$TeICl, undergo to yield several new diaryl tellurium(IV) pseudohalide derivatives e.g. Ph$_2$TeICN and Ph$_2$Te(CN)$_2$[205].

The synthesis of [HOS$_3$(CO)$_{10}$](M-TeC$_6$H$_4$OMe) by the room temperature. Reaction of [(Ph$_3$P)$_2$N][HOS$_3$(CO)$_{11}$] with [(COMe)C$_6$H$_4$]$_2$TeCl$_2$ and its conversion into [OS$_3$Ten(CO)$_9$] under thermolysis are reported[206].

Reactions of diaryl telluroxide R$_2$TeO (R = Ph, 4-MeOC$_6$H$_4$) with Me$_3$S$^+$OI$^-$ in MeCNH$_2$O gave 61-72% (R$_2$TeI)$_2$O. Heating R$_2$TeO (R=Ph, 4-MeO-C$_6$H$_4$,4-tolyl)with MeI gave 82.99% R$_2$TeI$_2$. Treating R$_2$TeO (R=Ph, 4-

$Me_2CHC_6H_4$) with $(R'O)_2SO_2(R'=Me,Et)$ gave 91-96% bis (diarylakoxytellurium) sulfates $[R_2Te(OR') O]SO_2$[207.]

Reactions of $4-MeC_6H_4COCH_2Bu_2$ with Se and Te gave $(4-MeC_6H_4COCH_2)_2XBr_2$ $(X=Se,Te)$. Adducts of $(4-MeC_6H_4COCH_2)_2$ XBr_2 were prepared with morpholine, piperidine and Me_2NH. Condensation of($4-MeC_6H_4COCH_2)_2XBr$ with diamines, hydrazines and semicarbazides gave heterocycles and $[RN=C(C_6H_4Me-4-CH_2)_2XBr_2$ $(R=OH, NHCSNH_2, NHCONH_2, NHphNHC_6H_3(NO_2)_2-2,4]$. The prepared compounds were tested for bacterial and fungicidal activity 208.

$R_4Te(R= Me, Bu,Me_3SiCH_2,$ vinyl) were prepared by treating $TeCl_4$ with equivalent LiR or RMgX and decomposed thermally and photolytically via a free radical pathway while $(CH_2=CH)_4$ Te decomposed by moncouple reductive elimination. Treating $TeCl_4$ with 4 equivalent Me_3CLi and $CH_2=CH_2MgCl$ gave the corresponding R_2Te directly $(Me_3C)_2$ Te was also isolated as a minor product from the reaction of Me_3CTeLi with Me_3CLi in THF. $(CH_2 =CHCH_2)$ Te was prepared form Li_2Te and 2 equivalent $CH_2 = CHCH_2I$ in THF. These compounds were characterized by ^1H, ^{13}C and ^{125} Te NMR spectroscopic[209].

$TeR^1(S_2CNR_2)n$ $(R^1 = 2-PhN:NC_6H_4CN, R_2 = Me, Et$ $PhCN_2$ n=1,3) were prepared and characterized by ^{125}Te NMR data indicate dissociation of $TeR^1(S_2CNR_2)n$ (n=3) to $TeR^1(S_2CNR_2)$ n (n=1) in solution and ^{125}Te mossbaurer data suggest that $TeR^1(S_2CNR_2)n$ (n=3) are better formulated as charge transfer compounds $TeR^1(S_2CNR_2) S_2 (SCNR_2)_2$. The crystal and mo-

(62)

lecular structure of TeR^1 (S$_2$CNR$_2$)n (R=Me, n=1) determined by X-ray diffraction showed a distorted planar enviro\nment for Te[210].

I.R. indicates that the undentate NO$_3$ group in Ph$_2$Te(NO$_3$)$_2$L (L = pyridine, N-Oxide, Ph$_3$PO, DMSO, 1-methyl-2-pyrrolidinone, tetramethylpiperidine, Me$_2$NCH$_2$CH$_2$NMe$_2$ on 2,2-bipyridine formed from Ph$_2$Te(NO$_3$)$_2$ and L is covalently bonded[211].

Synthesis of bis(alkyltelluro) methanes are reported. ^{125}Te NMR chemical shifts measured in CDCl$_3$ are reported relative to neat Me$_2$Te and range from 213.5 ppm for (MeTe)$_2$CH$_2$ to 713 ppm for (Me$_3$(Te)$_2$CH$_2$). The dihalides of bis(methyltelluro) and bis(phenyl telluro) methane were prepared and yield chemical shifts in the relatively narrow range of 786 ppm for CH$_2$(TeMe)$_2$ to 834 ppm for CH$_2$(TeClMe)$_2$. The trends in the chemical shifts and the ^{125}Te mossbauer parameters are compared with those previously reported for the diorganyl tellurides and their halides[212].

^{19}F chemical shifts were obtained for 4-RC$_6$H$_4$XC$_6$H$_4$F-4 (R = Me$_2$N MeO, Me, H, F, Cl, Br, X=Te, TeCl$_2$) and ^{13}C chemical shifts were obtained[213].

ΔThe ^{125}Te NMR shifts for Ph$_4$Te(508.9 ppm) and bis (2,2'-biphenylene) TeI (486.3) ppm were measured at ambient temperature together with the ^{125}Te mossbauer parameters for the heat solids. Ph$_4$Te (δ 0.09, Δ5.60 mmS^{-1} I(δ 0.42, Δ6.40 mmS^{-1}) at 4.2K. These results are compared with those for other

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organotellurium compounds. The mass spectra of these compounds are also reported)[214].

^{125}Te mossbaur parameters were measured at 4.2^{0}K for p-RC$_6$H$_4$)$_2$TeF$_2$, p-RC$_6$H$_4$TeF$_3$, (p-RC$_6$H$_4$)$_2$Te(OAC)$_2$, (p-RC$_6$H$_4$)$_2$Te(OBu)$_2$, (R = H, EtO, MeO, Me), Ph$_2$MeTeI and PhMe$_2$TeI. The structure of difluoride was the similar to that of other halides whereas the coordination of trifluorides was different from that of the other trihalides. The dicarboxylates had parameters similar to that of dihalides. Suitable changes in the coordination about Te occurred with changes in the acyl ligand[215].

The reaction of thirteen aliphatic ketones with TeCl$_4$ was studies with ^{1}H, ^{13}C and ^{125}Te NMR. TeCl$_4$ adds electrophilically to the α-carbon of the enol to form keto tellurium trichlorides. Unsymmetrical ketones gave mixture of isomeric ketonyl tellurium trichlorides Stearic hindrance determined which Ketonyltellurium trichlorides form. Except for the ketonyl tellurium trichloride form 2-butanone Te reacts preferentially with the least substituted α-C. Six methyl alkyl ketones also yielded appreciable amount of diketonyl tellurium dichlorides. In all diketonyl tellurium dichlorides, Te is bonded to less hindered methylene carbons[216].

^{35}Cl NQR spectra are reported for RR^{1}TeCl$_2$(R = Ph, R^1 = Cl; R = Ph, R^1 = 3, 4-(MeO)$_2$C$_6$H$_3$, R = R^1 = 3, 4- (MeO)$_2$C$_6$H$_3$)splittings in the NQR spectrum of PhTeCl$_3$ are consistent with the reported polymeric structure of this compound. With a square pyramidal six coordination polyhedron for Te,

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decreasing Te-Cl bond length corresponded to increase in NQR frequency of the participating Cl atom. A correlation between NQR frequency on Te-Cl bond length was valid for organotellurium chloride without bridging Cl atom[217].

Bis(P-phenoxy phenyl) tellurium dichloride is monoclinic space group $p^{21/C}$ with a = 8.063(27), b = 21.695(5), c = (12.622)2A^0 and β = 101.57(2^0) Z = 4. Final R = 0.055 for 2135 reflections. At coordination are given, the compounds adopts a primary four coordinate geometry based on distorted trigonal bipyramidal with an equitorial lone pair. A weak Te-Cl secondary interactions links, the molecule into centrosymmetric dimers[218].

Crystals of bis (4-phenoxy-3-methylphenyl) tellurium(IV) dichloride are monoclinic space group $p^{21'c}$ with a = 14.651(3), b = 12.787(3), c = 8.279(2)A^0 and β = 92.64(2)^0 Z = 4. R = 0.0298 for 1907 observed reflections, at parameters are given. The coordination about Te is trigonal bipyramidal with a vacant equatorial position Cl atoms axial and aryl ligands equatorial. An intermolecular OH-Cl hydrogen bond occurs in the crystal. But unlike other R_2TeCl_2 structure, there is no significant secondary bonding between Te and Cl in neighbouring molecules[219].

The (p-phenoxy phenyl) tellurium trichloride is triclinic space group p^1 with a = 8.521(2), b = 10.917(2), C = 14.813 (2) A^0 α = 81.84 (1) β = 83.38, and γ = 88.41(1)^0, Zn = 2. The final R = 0.0359[220].

The (p - bromophenyl) dichloro (Phenyl) tellurium (IV) is triclinic space

group p_1 with a = 11.257(7), b = 10.817(4), c = 12.358(5)A^0 α = 82.61(4) β = 80.72(5) and γ = 69.38(4)^0 Z = 2(2 mole) for dc = 2.067 and do = 2.06 final R = 0.048, Rw = 0.052 for 3428 reflections. The structure consist of discrete tetramers in which individual molecules are linked through weak Te-Cl interactions[221].

The dichloro bis (p-methoxyphenyl) tellurium (IV) i.e., TeCl$_2$ (C$_7$H$_7$O)$_2$ is triclinic space group p-l with a = 10.245(5), b = 12.480(94), c = 13.654(4) A^0 α = 109.22(2) β = 80.42(3) and γ = 77.30(3)^0 do = 1.75 and dc = 1.76 for Z = 4 final R = 0.028 for 3406 unique observed reflections. At coordinates are given. The structure consists of isolated step like tetramers in which two independent molecules and their centrosymmetric equivalents are linked through Te - Cl secondary interactions the Te-Cl bonds occupy the equatorial and axial positions, respectively in the saw-horse structure. The Ph rings are in a propeller arrangement[222].

The tetrakis(L-hydroxy ethyl) dithiacarbamato tellurium(IV) i.e., C$_{20}$H$_{40}$N$_4$O$_8$,S$_8$Te is triclinic space group PI with a = 9.008(2), b = 17.194(4), c = 14.501(2)A^0 α = 127.38(2), β = 9.60(2) γ = 97.13(2)^0 Z = 4 for dc = 1.654, R = 0.042 and Rw = 0.045 for 3482 reflections. The central Te is bonded to all eight atoms in a highly distorted dodecahedral configuration. The two plannar trapezoids, each contain a Te-S bond lengths are 2.637(4) – 2.857(4) A^0 the average being 2.738 (4) A^0. The extensive H-bonding of the terminal OH groups 2.678 (13)-2.676 (14)A^0 hinderd the autoredox reaction in TeL$_4$ and also pro-

vides stability for the crystal packing[223].

$(C_6H_5)_2TeF_2$ is monoclinic space group C_6 with a = 11.088(6), b = 20.040(1), c = 13.208(5)A^0 and β = 109.07(4)^0 Z = 4 (2 moles/Z) paris of crystallorgraphy independent molecules are linked by two weak secondary Te-F intermolecular bond. The structural model was refined by full matrix least squares to R = 0.035 for 162 reflection. At coordinates are given. The stereochemistry of primary bonding about Te is trigonal bipyramidal as for other R_2TeX_2 species and is compared with that of of $(Ph_2)TeF_2$. The difference in the stereochemistry of the primary bondigng about Te can be attributed to the influence fo the more electron withdrawing C_6H_5 group, and relates to different secondary bonding and the crystal packing [125]Te NMR coupling constants are reported for this and two related compounds previous [125]Te mossbauer data are discussed with regard to the structure[224].

The bis(2-hydroxy ethyl) dithiacarbamato diiodo tellurium(IV) i.e., $Te(C_5H_{10}NO_2S_2)_2I_2$ is triclinic space group PI with a = 10.740(7), b = 11.536(6), c = 11.000(8)A^0 α = 108.90(5) β = 121.94(5) and γ = 90.86(5^0) dm = 2.29 and dc = 2.316 for Z = 2, R = 0.062. The atomic parameters are given. The Te atom is seven coordinated to 4 S atoms to two axial I atoms and to an intermolecular bridging I in a distorted pentagonal bipyramidal geometry. The 2S atoms in each bidentate ligands forms unequal bonds. The dithiacarbamates parts of the two ligands are planar[225].

(67)

Crystals of $Ph_2Te(S_2CNEt_2)_2$ are monoclinic; one modification has space group pz_1. A 2nd modification has space group C2/C. Crystals of $Ph_2Te[S_2(OEt)_2]$ are orthorhombic. All three structure are monomeric and contain a stereochemistry active lone pair at the Te' atom making it effectively, seven coordinated in each cases[226].

Crystal structure analysis shows that $(Ph_2TeNCS)_2O$ is molecular in the solid states. The molecule has two fold symmetrical, with rotation axis passing through O atom and bisecting the Te-O-Te angle. The ether like Te-O-Te moiety is bent $121.4(4'')$ with Te-O cistance of 1.985(4) A^0. An intermolecular Te-S contact at 3.416 (3) A^0 completes a square pyramidal geometry around the Te atom and links the molecules into chains running parallel to the C-axis. The Te-N bond distance 2.40(1) A^0, indicates a tendency towards ionic character in the bond[227].

X-ray crystal structure of $[(C_6H_5TeCl_2)_2]_2CH_2$ and $(TeCl_3)_2CH_2$ were also determined[228].

The crystal structure determination of $Ph_3Te(S_2CN)(CHMe_2)_2$ indicates a most unusual dimeric structure in which the lignand can be considered as acting as bridge with very long Te-S bonds. The immediate environment about each tellurium atom can be described as that of a distorted octahedron. The three Te-C(phenyl) bonds are mutually cis with two long Te-S bonds of similar length and a lone pair completing the octahedron[229].

(68)

Reactions of Te(IV) with excess phenylene thiourea(L) in aqueous methanolic HCl gave $[TeL_4]Cl_2.2HCl$. The crystals are monoclinic space group p [21·c] a = 13.939(5), b = 6.52C(9), c = 4.873(2)A^0 and β = 100.29(4^0) d (calculated) = 1.651 gem^{-3} Z = 2 Final R = 0.055 and Rw = 0.056 for 918 independent reflections. The Te atom is bonded to 4 phenylene thiourea S atoms in a square planar arrangement with Te-S(1) = 2.678(6) Te-S(2) = 2.674(5)A^0 and S(1) Te-S(2) =90.5(3^0). The ligand behaves as a thione or atoms remains outside the coordination spehere of the Te and stabilize the packing arrangement in the unit cell through H-bondings to N atoms[230].

The reactions of Ph_2TeCl_2 with Schiff bases $O-HOC_6H_4(R) = NNH_2$ (R = H,OH) and hydrazine derivative Fig. 31(R^1 = H, Cl, Br, R^2 = H, Me) gave Ph_2TeL_2 and $4Ph_2TeL^i$ respectively . The compounds exhibited a pseudoctahedral structure in which the which the Te atom was in a sp^{3}d^3 hybridized state resulting in pentagonal bipyramidal geometry with stereochemistry, inert lone pair of electron occupying an equatorial position[231].

Fig. 31

(69)
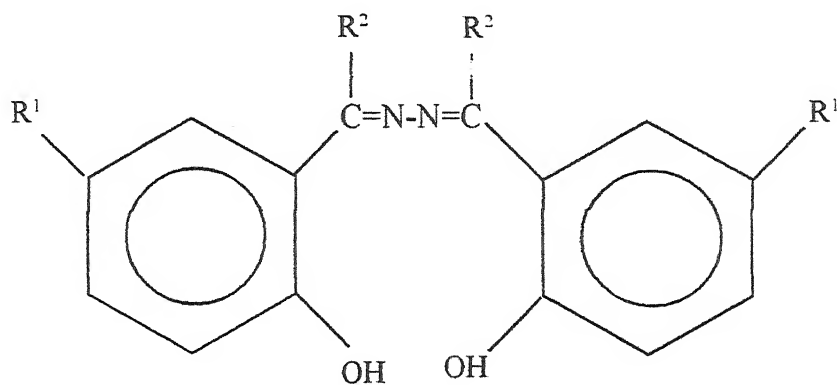
Some diorganotellurium(IV) complexes $(4-RC_6H_4)_2TeL$ [R = H, OMe, Oet], a tetradentate and tridenate Schiff bases derived from $(MeCO)_2CH_2$ and $H_2N(CH_2)nNH_2$ or $2-H_2NC_6H_4XH$, (n = 2,3 X = 0, S) were prepared and characterized by elemental analysis, conductance;molecular wight, I.R. and ^1H NMR data[232].

RR[1]TeSalen (R = p-R[2]OC$_6$H$_4$) (R[2] = Me, Et); R[1] = P-C$_6$H$_4$NMe$_2$, CH$_2$COCH$_3$ or CH$_2$Bu), and salen is the dianion of N, N[1] – ethylene bis (salicylideneimine were synthesized. I.R. and PMR spectral data established metal ligand bonding and the resulting geometry of the complex[233].

α-lithio derivatives of furanthiophene benzo(6) thiophene, pyridine and M-tosyl pyroll and diodole as well as 4-lithio dibenzo thiophene react readily with Te in THF representative conversions of the resulting heterocyclic Li tellurolates to ditellurides alkyl tellurides and telluroacetate are reported[234].

Several sulfonamide Schiff base complexes of the Te(IV) were prepared and characterized using conductivity measurements and I.R. and NMR spectra, elemental analysis confirmed a 1:2 (Metal-Sulfonamide Schiff base) stoichiometry most of the complexes proved to be biologically active (antibacterial hypoglymeric antiinflammatory) as evidenced by pharamacological tests[235].

Treating iminophenols(Fig.32) (R = R-OMe, 3-F, 4-Br; R[1] = H, O$_2$N) with Me$_2$Te(OMe)$_2$ gave 80-93% Fig.33 compounds (same R,R[1])[236].

(70)
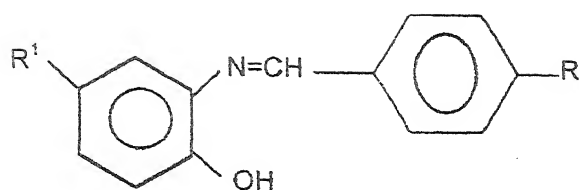
Fig. 32
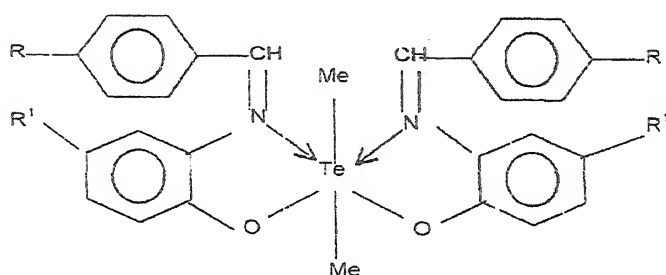
Fig. 33

Square pyramidal complexes $PhTeCl_3R^1CR^2:NNHCSNH_2$($R^1$ = Ph, 2-HOC_6H_4, R^2 = H, Me) were prepared. Other synthesized compounds were $Ph_2TeCl_2.R^1CR^2$: $NNHCSNH_2$ and $(4-R^3C_6H_4)_2.Ph.CH:NNHCSNH_2$ (R_3 = Me, OMe)[237].

A wide series of diorganyl diaryloxytelluranes e.g., (R = Me, R^1 = H, 4-NO_2, 5-NO_2, R^2 = 4-NO_2, 3-NO_2, 4-Br, H,4-Me, 4-MeO, 4-NMe^2, R = CH_2Ph4-MeC_6H_4, R^1 = H, R^2 = 4-MeO) having an azomethine function in the position ortho to the Te atom have been synthesized by the reaction of diorganyl dimethoxytelluranes with benzylidene o-aminophenols. The X-ray structure of dimethyl-bis [2-(4-nitrobenzalideneimino)phenyloxy] tellurane (R = Me, R^1 = H, R^2 = 4-NO_2) indicates the presese of an intramolecular Te-N coordination

(71)

bond.

Accoridng to the dpole moment data and the ^1H, ^{125}Te and ^{14}N NMR spectra compounds (excluding those with $R^2 = 4\text{-}NO_2$) retain the Te-N coordination in nonpolar solvents[238].

The reactions of thiosemicarbazones and semicarbazones of benzaldehyde, salicyldehyde, acetopheone and 2-hydroxy acetophenone with $TeCl_4$ give $Te(HL)Cl_4$, $TeCl_3$ and Te_2LCl_7 (HL = semicarbazone or thiosemicarbazone). The structural features of these Te derivatives are explored by I.R. ^1H, ^{13}C and conductance (in MeCN) measurements and structure based on octahedral arrangement of ligand around Te are proposed. The presence fo facial and meridian isomer in equilibrium is indicated in some cases. The complexation occurs through S/O. The nitrogen of the CN group of O^- (if present on benzene ring) TeL_2Cl_7 seen to have Cl bridged and octahedrally coordinated Te^{239}.

(IV) Compounds in Oxidation State(IV)

This oxidation state of tellurium is not very common. Till 1974, only $(C_2F_5)TeF_4Cl$ and $(C_2F_5)_2TeF_4$ were reported by Desjardins[240]. Later on, CH_3TeF_5 was prepared [241]. The presence of some tellurium fluoroanions $TeF_7{}^{2-}$ [242], $TeF_8{}^{2-}$ [242] and $TeO_2F_4{}^{2-}$ [243] has also been established by IR and Raman spectra.

The reactions of phenyl tellurium(VI) fluorides $PhTeF_5$, trans-$[Ph_2TeF_4]$ and mer-$[Ph_3TeF_3]$ with alcohol and amines or their trimethyl silyl derivatives are known. The products $[PhTeF_4X]$, $[Ph_2TeF_3X]$ and $[Ph_3TeF_2]$ (X = OMe,

NMe$_2$, NEt$_2$) were characterized by ^{19}F NMR spectroscopy and disomeric structures are assigned on the basis of their NMR spectroscopy samples of trans-[Ph$_2$TeF$_4$] contain small amounts of cis-[Ph$_2$TeF$_4$][244].

The hydrolysis fo PhTeF$_5$, trans-[Ph$_2$TeF$_4$] and mer-[Ph$_3$TeF$_3$] is known. The hydrolysis products (PhTeF$_4$OH, Ph$_2$TeF$_3$OH and Ph$_3$TeF$_2$OH, respectively) were identified by ^{19}F NMR and mass spectrometry and in the case of Ph$_3$TeF$_2$OH by X-ray crystallography Ph$_3$TeF$_2$OH has nonequivalent F atoms and the condition under which stereoselective F exchange occurs are known. The coordination about Te is octahedral with two Ph groups trans to each other and the third ph trans to an F atom. The molecule exhibits the longest known Te(VI) F bond 2.011(2) A^0. This same F which undergoes the more rapid exchange in solution is involved in H-bonding in the crystal, linking centrosymmetric related molecule into dimmers where OH-F is 1.90(3) A^0 < O-H-F is 1.77(4)^0 However, H-bonding is not responsible for the stereoselective F exchange in solution[245].

A series of phenyl tellurium(VI) fluoride PhTeF$_5$,Ph$_3$TeF$_3$, Ph$_3$TeF$_2$Cl, and Ph$_4$TeF$_2$ were prepared by oxidative fluorination of Te(IV) compounds with XeF$_2$. The compounds were characterized by elemental analysis, ^{19}F and ^{125}Te NMR mass spectra[246].

The reaction of TeMe$_4$ with XeF$_2$ in MeCN yielded the new compound cis-TeF$_2$Me$_4$ in 87% yield. Difluorotetramethyl tellurium(IV) has been charac-

(73)

terized by Mass spectroscopy, ^{1}H, ^{13}C, ^{19}F and ^{125}Te NMR spectra, methylation of TeF_2Me_4 with dimethyl zinc at reduced temperature proceed smoothly in diethyl ether to generate $TeMe_6$ in 68% yield. Hexamethyl tellurium is more thermally stable than $TeMe_4$[247].

$(CH_3)_2TeI_4$ is triclinic, space group PI, with a = 7.640(3), b = 12.600(5), c = 6.592(3)A^0 α = 82.82(3), β = 106.54(3) and γ = 106.45(3)^0 d(cald) = 3.832 for Z = 2. The structure was defined by least square to a final R_1 = 0.061. I-I bond (2.748-3.456 A^0) and weak Te-I bonds (2.809-3.957 A^0) and does not contain Te(IV)[248].

Some other organotellurium compounds which have not been included n the above discussion may be classified as below:

(i)   Tellurium ylides

(ii)   Heterocyclic tellurium compounds

(i) Tellurium ylides

This is a different group of organotellurium compounds. Sadekov prepared a number of tellurium ylides by reacting aryltellurium halides and 1,1-dimethy 1 - 3, 5 - cyclohexanedione in boiling benzene containing triethylamine[249-250].

$(R=H, CH_3, OCH_3)$
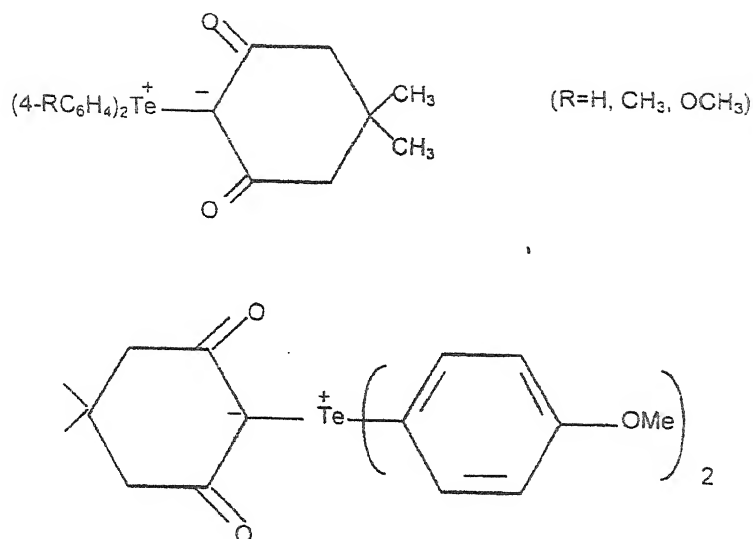
Fig. 34

The compound shown in Fig 35 synthesised by Freeman[16] in 1970 is the only other tellurium ylide known .
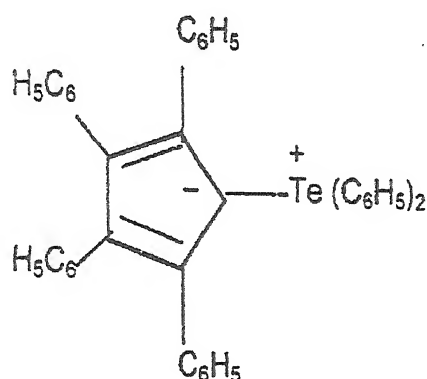
Fig. 35

(ii) Heterocyclic tellurium Compounds

New tellurium heterocyclic chemistry has been summarized[251]. Telluraphthalic anhydrides (Fig.36) were obtained by treating $NaBH_4$ with Te followed by phthaloyl chloride[252]. several five and six membered, 1,1-dihalogeno-1-tellura compounds have been prepared and their properties studied[253-259]. Treatment of sodium phenyl acetylide with tellurium in DMSO gave the ditellurols (Fig.37)[260].

(75)
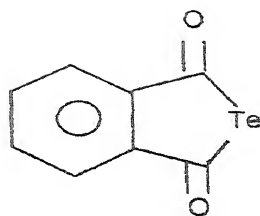
Fig. 36
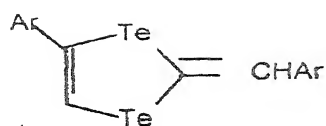
Fig. 3 7

When equimolar amounts of phenoxtelluride and its 10, 10-di-nitrate were dissolved in dichloreomethane a solid (Fig.38) products separated[261].
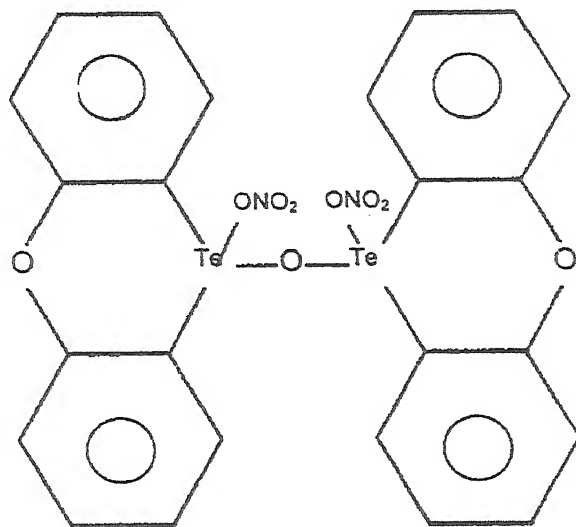
Fig. 38

Some new heterocyclic tellurium rings synthesized are shown in Fig. 39 with references shown in brackets:
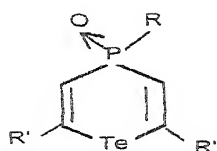
(Ref. 264)
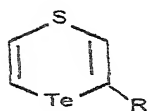
(Ref. 265)
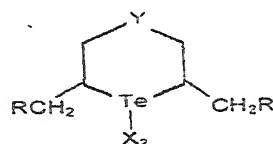
(Ref. 266)
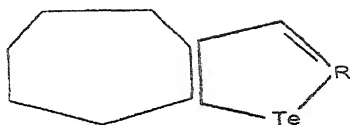
(Ref. 267)
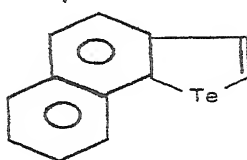
(Ref. 267)
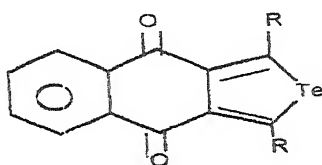
(Ref. 268)
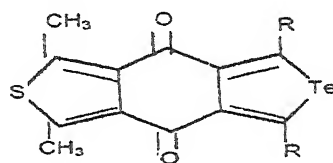
(Ref. 268)

A review with 661 references mainly for 1981 of the chemical and properties of monocyclic thiophenes, benzofused thiophenes, thiophene analogous of polycyclic aromatic hydrocarbons, thiophene fused to 5-and 6- membered hetero-atomic ring selenophenes and tellurophenes is reported[262-265].

In last few years some new organotellurium complexes have been synthesized. Cyclopentadienyl metal teflate (OTeF$_6$) complexes[266]. Reactions of $[M_2(CO)_{10}]$ (M = Mn or Re) with xenon bis [pentafluorooxo-tellurate (VI) and selenate (VI)][267], synthesis and characterization of monomeric telluro complexes of zinc and cadmium. Crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazolinyl) phenyl] ditelluride,[268] synthesis and characterization of Novel Chiral ortho-Tellurated complexes derived from (s) -1-(Dimethylamnio) ethyl Benzene. Crystal and Molecular structure of {2-[(S)-1-(Dimethyl amino)

(77)

ethyl] phenyl[1]} tellurium trichloride[269].

Synthesis, spectroscopic and structural studies on rhodium (I) and (III) and iridium (I) and (III) selenoether and telluroether complexes involving organometallic co-ligasnds[270], synthesis and characterization of tris (trimethylsilyl) methylaluminium chalcogenides $[RAl(\mu_3\text{-}E)]_4$ (R = $(Me_3Si)_3C$; (E = Se, Te) and 1-Azaallylagallium chalcogenides $[R'Ga(\mu_2\text{-}E)_2$ (R[1] $=(Me_3Si)_2C(Ph)C;(Me_3Si)N$; E= S,Se, Te)[271], bis (tetraisopropyl cyclopentadienyl nickel) dichalcogenid : complexes of the Novel $[\{CpME\}_2]$ Type (E = S,Se, Te)[272]. Monooxytellurane (IV) derivatives ($\{10\text{-Te-}4(C_3O)\}$]). Sythesis and molecular structure of triaryltelluronium carboxylate compounds[273], organotellurium precursors for metal organic chemical vapour deposition (MOCVD) of mercury cadmium telluride (MCI)[274]. Stereochemical aspects of Tellurium complexes with sulfur ligands: Molecular compounds and supramolecular associations[275].

A very few work have been done on organotellurium complexes with monocyclic ligands[276-280].

A very few organotellurium compounds with schiff base ligands are known but the reaction of organotellurium compounds (R_2Tex_2) with 3 - mercapto - 4 - salicyldimino - 1,2,4 - triazole; 3 mercapto - 4 - β - isatinylimino - 1,2,4 - triazole and α - phenyl salicylaldimino - methyl - β - naphthol are not known.

The chapters in the thesis have been organized to provide an easy access to the formation available on the topics treated. The first two chapters deals with the general introduction of organotellurium compounds, materials used and the experimental techniques used to characterised and the synthesised compounds. In the third chapter the various organotellurium (IV) compounds of the type (R_2Tex_2) where $[(C_6H_5CH_2)_2TeI_2]$; $[(C_6H_4)_2TeCl_2)]$; $[(p\text{-}MeOC_6H_4)_2TeCI_2]$; $[(p\text{-}Me_2NC_6H_4)C_6H_5TeCl_2)]$; $[(p\text{-}Me_2NC_6H_4)$ $(p\text{-}MeOC_6H_4)TeCl_2)]$;$[(p\text{-}Me_2NC_6H_4)$ $(p\text{-}EtOC_6H_4)TeCl_2)]$; and $[(CH_3)TeI_2]$3-mercapto-4- salicyldimino - 1,2,4 - triazole have been studied. in the IV and V chapter

the various organometallic compounds of the type R_2TeX_2 (where - $[(C_6H_5CH_2)_2TeI_2]$;$[(C_6H_4)_2TeCl_2)]$;$[(p\text{-}MeOC_6H_4)_2TeCI_2]$;$[(p\text{-}Me_2NC_6H_4)C_6H_5TeCl_2)]$; $[(p\text{-}Me_2NC_6H_4)(p\text{-}MeOC_6H_4)TeCl_2)]$; $[(p\text{-}Me_2NC_6H_4)(p\text{-}EtOC_6H_4)TeCl_2)]$; and $[(CH_3)TeI_2]$ with 3-mercapto-4-β−isatinylimino - 1,2,4-triazole and with............ 1,2,4,-triazole respectively have been studied to establish reaction product geometry and structure.

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CHAPTER - II

STARTING MATERI-
ALS, ANALYTICAL
METHODS AND
EXPERIMENTAL
TECHNIQUES

This chapter deals with the source from where various starting materials have been obtained. There are several physico-chemical methods for the study of newly synthesized complexes are also given.

Materials

(i)   *Solvents :* E.Merck(L.R.Grade) and Ranbaxy solvents were used after purification and   drying by conventional methods[1].

(ii)   *Tellurium Powder :* Finely divided tellurium powder received from Aldrich was used without further purification.

(iii)   *Tellurium tetrachloride :* Anhydrous tellurium tetrachloride was obtained from B.D.H. Other stating materials used in the present investigation, prepared either from reported methods or obtained from commercial sources as listed in table 1 and were used after purification.

Table1: Specifications and abbreviaton of materials employed.

Name	Source	Abbreviation
Salicylaldehyde	SISCO	-
Isatin	SISCO	-
β-naphtol	BDH	-
3-mercapto-4-amino 1,2,4-triazole	BDH	-
α-Phenyl-amino-methyl-β-naphtol	Aldrich	-

Experimental Techniques

A brief description of the techniques used in the investigation of the newly synthesised complexes described in the present work are given below:

1. Infrared Spectroscopy
2. Molar Conductivity Measurement
3. Elemental Anaysis and
4. X-Ray Photoelectron Spectroscopy

When infrared light is passed through a sample of a compound, some of the frequencies are absorbed, while other frequencies are transmitted through the sample without being absorbed. If we plot the absorbance or transmittance against frequency, the result is an infrared spectrum. Infrared spectrum of all these complexes were re corded in KBr or CsI on a perkin Elemer 621 and /or 782 spectrophotometer.

$$Am = \frac{\text{Cell constant X conductance}}{\text{Concentration solute expressed in mol}^{-1}\text{ cm}^2}$$

Conventionally solution of 10^{-3} M strength are used for the conductance measurement. The electrical conductivities of 1×10^{-3} M solution in DMSO were obtained on digisun electronic conductivity bridge equilibrated at 25 ± 0.1^0C.

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligands as well as its complexes. Elemental analysis of C,H,N,O

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and Te were carried out on semimicro scale at central Drug Research Institute, Lucknow, India.

The X-ray photoelectron spectra i.e. XPS were recorded on a VG scientific ESCA-3MKII electron spectrometer at National Chemical Laboratory, Pune-8. The Mg Kα x-ray line(1253.6 eV) was used for photoexcitation. The $Cu2P_{3/2}$ (BE = 932.8 ± 0.2) and $Au4f_{7/2}$ (BE = 83.8 ± 0.1) lines were used to calibrate the instrument and $Ag3d_{5/2}$ (BE = 368.2 eV) was used for cross-checking[3]. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mn slit width. The reduced full width at half maximum (FWHM) at the $Au4f_{7/2}$ (BE = 83.8 eV) level under these conditions was 1.2 eV.

The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed in a gold metal gauze which was welded to nickel sample holder. The $Ag3d_{5/2}$ level (BE = 368.2 eV) obtained from this sample was sharp and did not show any observfable shift. Thus th e changing of the the sample if at all present was negligible. The spectra were recorded in triplicate in the region of the interest. In the most of cases the binding energies were reproductable within ± 0.1 eV.

Preparation of $(C_6H_5CH_2)_2TeI_2$

A mixture of benzylchloride (2.53g, 0.02 mol, tellurium powder (1.26 g, 0.01 mol and sodium iodide (3g, 0.02 mol) was heated under reflux at 110^0 C

for 40 hrs. The reaction mixture was extracted with dry chloroform, the chloroform extract concentrated and the residue recrystallised from chloroform-pet ether[4].

Preparation of $(C_6H_4)_2TeCl_2$

0.125 mol of biphenyl (19.25g) was heated with 0.100 mol $TeCl_4$ (26.89g). At 110°C HCl was evolved. The reaction was continued between 140-160°C till HCl ceased to evolved (~18hrs). The solid thus obtained was washed several times with pet-ether (60-80°C) to remove excess reactants and the product was recrystallised from dry acetone[5].

Preparation of Bis(p-methoxyphenyl) telluriumdihalide (p-MeOC_6H_4)_2TeCl_2

Tellurium tetrachloride (22.5g; 0.08 mol) and anisole (45.0 g; 0.4, 0.41mol) were heated for 6 hrs at 160°c and the mixture was concentraterd under reduced pressure to crystallization. The dichloride was recrystallized from cold acetonitrile[7].

Yield = 27.5 g; 80%

m.p. = 182 - 83° [Reported (182 - 183°)]

Preparation of p-dimethylaminophenyl(aryl) tellurium dihalides (p-Me_2NC_6H_4)RTeCl_2:

The title compounds were prepared by mixing aryltelluium trichloride

with dimethylkaniline at room temperature according to the following equation[8].

$$RTeCl_3 + \langle\bigcirc\rangle\!-\!N(CH_3)_2 \xrightarrow[-HCl]{24 \text{ hrs room temperature}} R-Te\!-\!\langle\bigcirc\rangle\!-\!N(CH_3)_2$$

(with Cl and Cl on the Te)
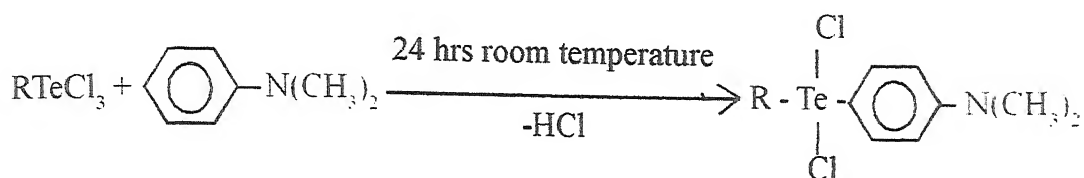
$(R = p\text{-}CH_3OC_6H_4,\ p\text{-}C_2H_5OC_6H_4)$

Preparation of [(p-Me₂NC₆H₄)(p-MeOC₆H₄)]Te and [p - Me₂NC₆H₄) (P - EtOC₆H₄]Te :

p-dimethylaminophenyl(p-mehoxyphenyl) telluride and *p*-dimethylaminophenyl (*p*-ethoxyphenyl) telluride were similary prepared by reduction of corresponding dichlorides and had m.p. 96^0c (reported $96\text{-}97^0c$) and 126^0c (reported $126\text{-}127^0c$)[9.8].

yield = 100%

Preparation of dimethyltellurium diiodide(CH₃)₂TeI₂

In a glass bulb of 150-200 ml copacity, was sealed a mixture of 10.0g (0.07 mol) of amorphous tellurium and 22.4g (0.15mol) of methyl iodide. The sealed bulb, was kept in a water bath at 80^0c for 36-48 hrs. The brittle red mars thus obtained, was powdered and extracted with chloroform. The mixture was filtered through a hot funnel to separate unreacted tellurium. The yield of dimethyltelluriumdiiodide based on the amount of crystalline solid obtained from the chloroform soluition, was about 53% It was recrystallized from a nonaquous solvent such as chloroform, benzene or acetone[10].

(110)

Yield = 17.0g(53%)

m.p. = 127^0(d)[Reported 127^0(d)]

Preparation of p- dimethylaminopheny(p-methoxy phenyl tellurium dichloride (p-Me$_2$NC$_6$H$_4$) (p-MeOC$_6$H4) TeCl$_2$:

p – methoxyphenyl tellurium trichloride (34.0g,0.10mol) was intimately mixed with N, N - dimethylailine (36.0g, 0.30 mol). The reaction was exothermic, and a transient bluish green colour appeared. After 24 hrs the mixture was extracted several times with methanol, leaving a yellow crystalline residue of the dichloride. The product was recrystallised from methanol or benzene/methanol as yellow prism[5].

Yield=32g(75%)

m.p. = $169\text{-}170^0$c[reported $170\text{-}172^0$c]

PrePararation of [(p-Me$_2$NC$_6$H$_4$)(p- EtOC$_6$H$_4$)]TeCl$_2$:

It was prepared similarly[8].

m.p. = $149\text{-}150^0$c[reported $153\text{-}154^0$c]

Preparation of 3-mercapto-4-β-Isatinylimino-1,2,4-trizole :

The compound is formed by reflexing 3-mercapto-4-amino-1,2,4-triazole with molar proportion of isatin in aqueous methanol.

$$N = C \underset{\underset{H}{\diagdown}}{\overset{\overset{SH}{\diagup}}{}} N - NH_2 \quad + \quad O = C \cdots \bigcirc$$

3-mercapto-4-amino   I satin
1,2,4 - triazole

3-mercapto-4- β - Isatinylimino - 1,2,4 - triazole
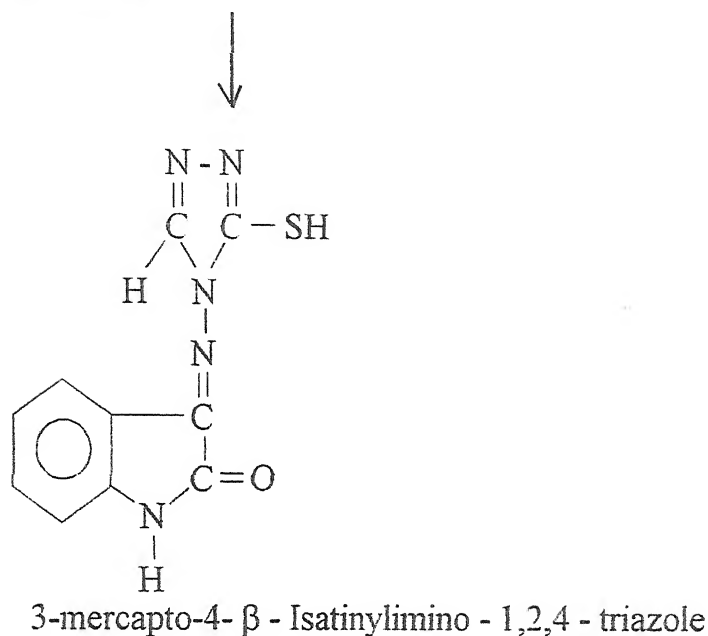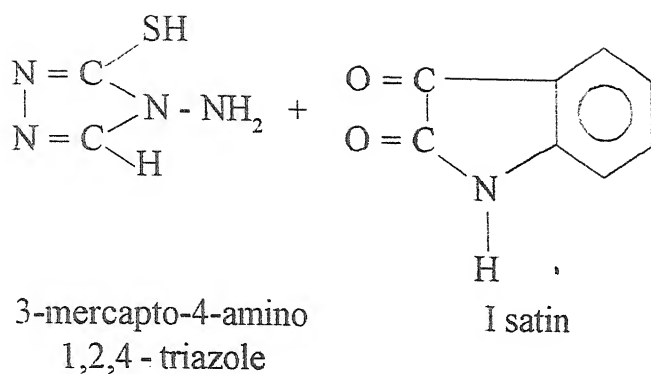
Procedure

About 11.6g of 3-mercapto-4-amino-1,2,4-triazole was dissolved in 50-60ml not aqueous methanol and treated with 14.8 g of isatin dissolved in 50-60 ml methanol. The resulting solution was refluxed for one hour when cream yellow product separated gradually. The product was collected on a filter, washed with aqueous methanol and dried in air. The Schiff base of isatin obtained from 4-amino-triazole is less soluble in methanol or ethanol but dissolves appreciably in pyridine and dioxane. The lignad is highly soluble in DMF. The product obtained by recrystallisation it with methanol. It was found to contain N =

28.41%. The title product required N = 28.3%

Preparation fo 3-mercapto-4-salicylaldimino-1,2,4-triazole:

The comound was prepared by condensing 3-mercapto-4-amino-1,2,4-triazole with equimolecular proportion of salicylaldehyde in aqueous methanol.

3-mercapto-4-amino
1,2,4 - triazole
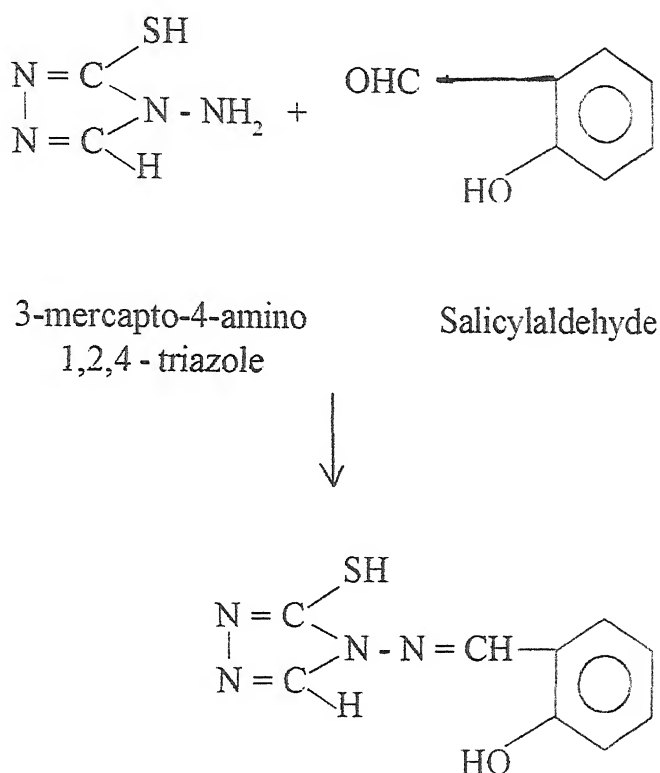
Salicylaldehyde

3-mercapto-4- Salicylaldimino - 1,2,4 - triazole

Procedure

About 11.6g of mercapto-4-amino-1,2,4-triazole was refluxed with 12.2g of salicylaldehyde in 60-70ml aqueous methanol containing 2-3ml glacial acetic acid for one hour. On refluxing, a clear solution was formed within 5-10 minutes from which crystallined needles separated gradually. The refluxate on cooling at room temperature deposited cream coloured product. The product was collected on a filter and recrystsallised with dioxan-methanol mixture. The

(113)

recrystallised product was collected on a filter, washed with methanol and dried in a desiccator over $CaCl_2$. the product on analyse was found to contain N= 25.34% The title product requires N=25.45%.

3-mercapto-4-salicylaldimino-5-methyl-1,2,4-triazole i.e.(5Me-salmtrH$_2$) and 3-mercapto-4-salicylaldimino-5 phenyl-1,2,4-triazole i.e.(5Ph-salmtrH$_2$) were prepared by same method as for 3-mercapto-4-salicyladimino-1,2,4-triazole; by taking 3-mercapto-4-amino-5methyl 1,2,4-triazole and 3-mercapto-4-amino-5phenyl 1,2,4-triazole respectively.

Preparation of α-phenylsalicylaldimino-methyl-β-napthol:

The compound was prepared in two steps by reported method:

  (a) Preparation of α-phenyl-amino-methyl-β-naphtol.

  (b) Condensation of α-phenyl-amino-methyl-β-naphthol with Salicylaldehyde.

  (c) Condensation of α-phenyl-aminomethyl-β-naphtol with salicylaldehyde.

  (d) α-phenyl-aminomethyl-β-naphthol was prepared by reacting β-naphthol with benzaldehyde and ammonia in hot ethanol.

β-naphthol　　　　Benzaldehyde　　　α-phenyl-amino-β-naphtol

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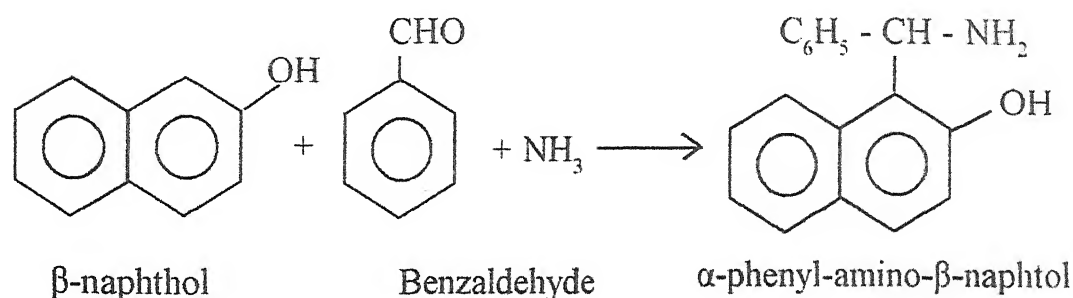
Procedure

About 21.2g o freshly distilled bezaldehyde was dissolved in 50 ml ethanol. Crystallined 28.8 g β – naphthol was dissolved in 150 ml hot methanol and taken in a three necked 500 ml round bottom flask fitted with a mecehanical stirrer. The solution was maintained at 90-95° and ethanolic solution of benzaledehyde and cone. ammonia (30 ml) were added dropwise from separating funnel to β naphtol solution. The addition of reactant were completed in half an hour while maintaining the temperature to 90-95°C and stirring to reaction mixture with mechanical stirrer. When the addition of benzaldehyde and ammonia was complete the resulting solution was refluxed for 4 hours on steam bath . After refluxing the volume of refluxate was reduced to ¼ by distilling the alcohol as a steam bath. The concentrated solution was mixed with 500 ml of cold water when white product separated. It was colleced on a filter. The residue was dried and extracted with ether the product obtained on evaporation fo ether was recrystallised with ethanol. M.P.Found : 244°c.

(b) Condensation of salicylaldehyde with α-phenyl –aminomethyl –β-naphthol easily yields the Schiff base.

α-phenyl – amino-methyl – β-naphthol

Salicylaldehyde

α-phenyl Salicylaldimino methyl - β - naphtol

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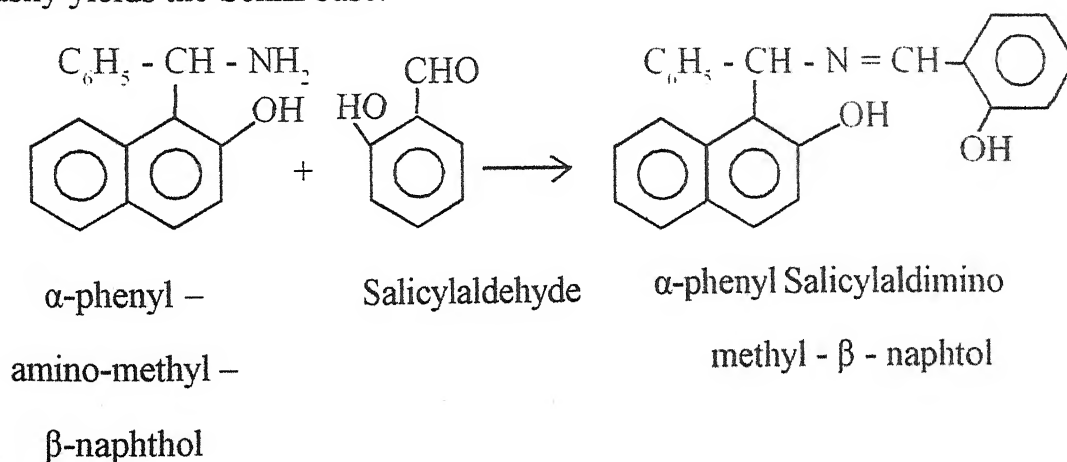
Procedure

About 12.2g salicyldehyde was dissolved in 20-30ml ethanol and added to ethanolic solution of 25g of α-phenyl-aminomethyl-β-naphthol dissolved in 50ml hot ethanol. The resulting solution was treated with 2ml glacial acetic acid and refluxed on steam bath for an hour when light yellow product separated. The product was collected on a filter and washed with ethanol. Found N= 3.81% and required for titled product N=3.96%.

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CHAPTER – III

"COMPLEXES OF R$_2$TeX$_2$ WITH 3 - MERCAPTO - 4 - SALICYLALDIMINO - 1, 2, 4 - TRIAZOLE"

"COMPLEXES OF R_2TeX_2 WITH 3 - MERCAPTO - 4 - SALICYLALDIMINO -1, 2, 4 - TRIAZOLE"

3-Mercapto-4-amino-1,2,4-triazole(I) is potential 'N' and 'S' donor ligand and its complexes with transition metals are well known[1-5]. The methyl derivatives 5-methyl-3-mercapto-4-amino-1,2,4-triazole(ii) and 5-phenyl-3 mercapto-4-amino-1,2,4- triazole (III) have same donor sites similar to parent ligand(I).
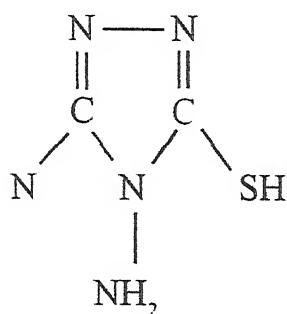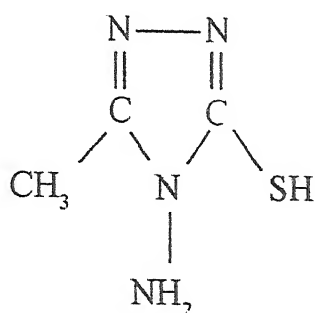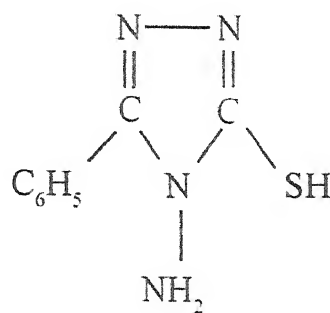
(I)   (II)   (III)

The NH_2 group of these triazole derivatives condenses with aldehyde or Ketone and forms Schiff base ligands with salicylaldehyde.
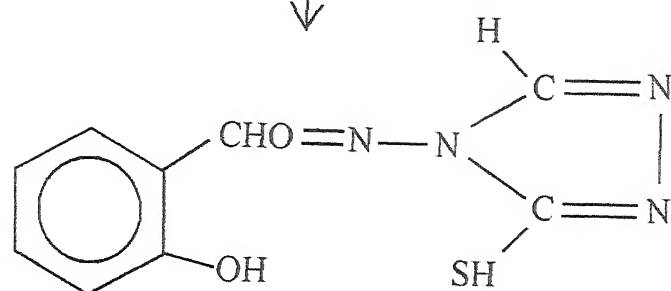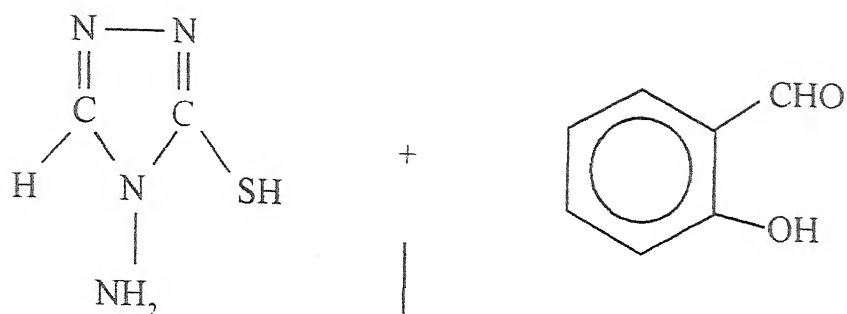
3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. abbreviated as (SalmtrH$_2$)
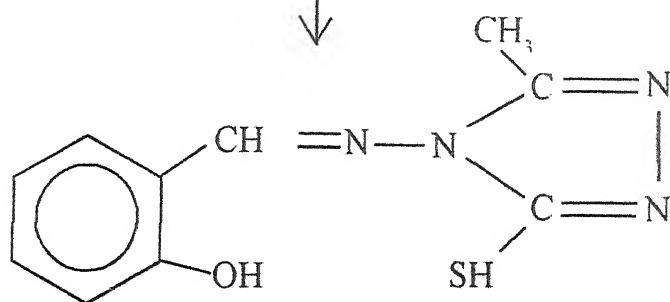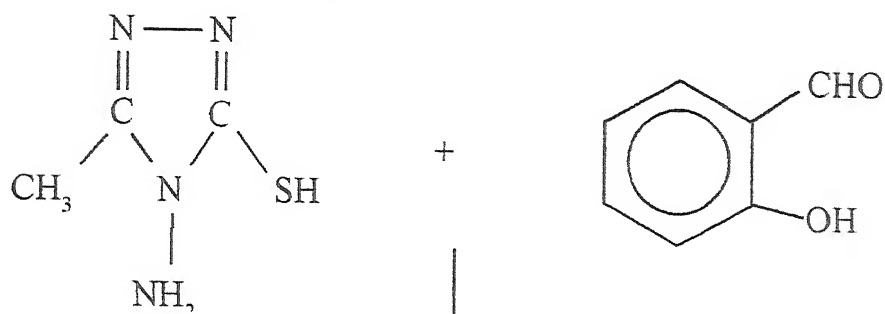
Schiff Base

5 - methyl - 3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. (5 - Me - SalmtrH$_2$)

(119)
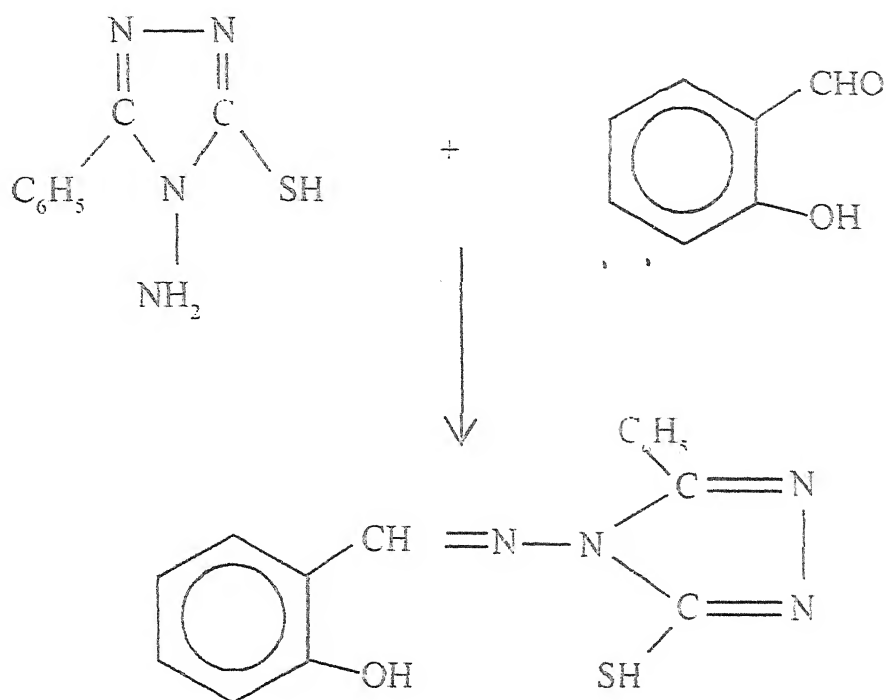
Schiff Base

5 - phenyl - 3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. (5 - Ph - SalmtrH$_2$)

Although various Schiff base ligands interaction with R$_2$TeX$_2$ have been studied, to know the geometry and significance of the produced complexes , the interaction of R$_2$TeX$_2$ with salmtrH$_2$ and its derivatives Schiff base ligands have been not studied, to know the site of coordination and geometry. This chapter deals with such type of study.

Preparation of [R$_2$Te(salmtr)] R$_2$Te(5-Me-salmtr)] and [R$_2$Te(5-Ph-sakmtr)] complexes:

The R$_2$TeX$_2$(1mmol) i.e.[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$]; [(C$_6$H$_4$)$_2$TeCl$_2$]; [(p-MeOC$_6$H$_4$)$_2$TeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)PhTeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)(p-

(120)

MeOC$_6$H$_4$)TeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$] and [(CH$_3$)$_2$TeI$_2$] was dissolved in dry methanol (30ml) and Schiff base ligand i.e. salmtrH$_2$ or 5-Me-salmtrH$_2$ or 5-Ph-salmtrH$_2$(1mmol) was mixed in this solution. The mixture was refluxed for 3-4 hrs. The solid product was obtained filtered product was washed with pet-ether and air dried.

Preparation of [R$_2$Te(salmtrH)$_2$] R$_2$Te(5-Me-salmtrH)$_2$] and [R$_2$Te(5-Ph-salmtrH)$_2$] complexes:

The R$_2$TeX$_2$(1mmol) i.e.[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$]; [(C$_6$H$_4$)$_2$TeCl$_2$]; [(p-MeOC$_6$H$_4$)$_2$TeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)PhTeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$]; [(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$] and [(CH$_3$)$_2$TeI$_2$] was dissolved in dry methanol (40ml) and Schiff base ligand salmtrH$_2$ or 5-Me-salmtrH$_2$ or 5-Ph-salmtrH$_2$(2mmol) was mixed in this solution. The mixture was refluxed for two hrs. The solid product was obtained filtered washed with pet-ether and air dried.

RESULTS AND DISCUSSION

The all prepared complexes – [R$_2$Te(salmtr)]; [R$_2$Te(5-Me-salmtr)]; [R$_2$Te(5-Ph-salmtr)]; [R$_2$Te(salmtrH)$_2$]; [R$_2$Te(5-Me-salmtrH)$_2$] and [R$_2$Te(5-Ph-salmtrH)$_2$] were found to be air stable. The observed molor conductance values of all the complexes in acetone were observed 20-30 ohm^{-1} em^2 mol^{-1} indicate that they all are non-electrolyte in nature (Table 2).

The IR spectra of 3-mercapto 4-salicylaldimino-1,2,4,-triazole i.e.

(salmtrH$_2$) contains a phenolic OH and a mercapto sulphur capable of existing in Retoenol tautomeric form:-
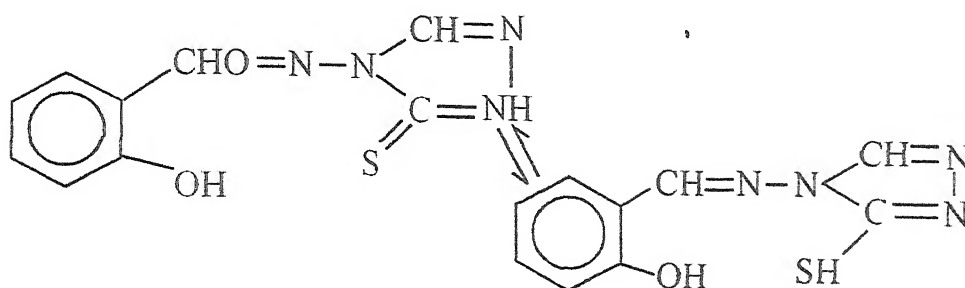
The IR bands position of ligand salmtrH$_2$ are listed in table the ligand displays a medium band at 3230 cm^{-1} asssignable to υ(OH) of phenolic hydroxygroup and sharp band at 3115 cm-1 attributable to υN-H group. The absence of υS-H in the region 2400-2850 cm^{-1} indicate that ligands exclusively exists in thion tautomer rather than thiol form. The free ligand displays υC=N aldimino part at 1615 cm^{-1}. The υC=N vibration is shifted to higher frequency
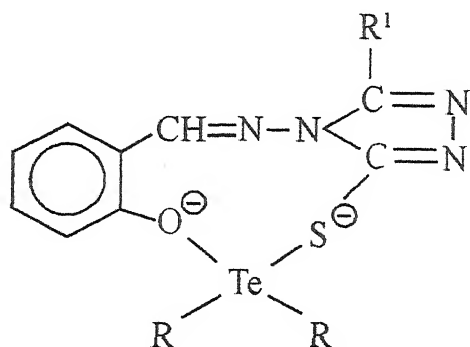
R^1 = H, Me, Ph

Structure of [R$_2$Te(Salmtr)], [R$_2$Te(5 - Me - Salmtr)]
and [R$_2$Te(5 - Ph - Salmtr)] complexes

(122)
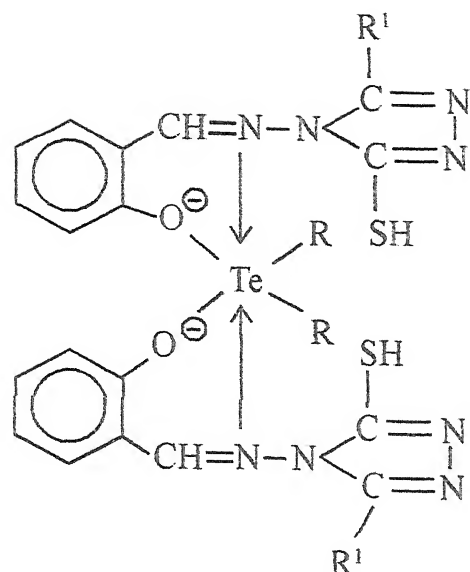
$R^1 = H, Me, Ph$

Structure of $[R_2Te(SalmtrH)_2]$, $[R_2Te(5 - Me - SalmtrH)_2]$
and $[R_2Te(5 - Ph - SalmtrH)_2]$ complexes

and observed as broad and strong bands due to mixing of $\upsilon C=N$ of triazole ring . The thioamide band I of free ligand is observed at 1536 cm^{-1} , Thioamide band II is observed at 1342 cm^{-1}. The $\delta(OH)$ of free ligand is assigned to a bond at 1320cm^{-1}. The $\upsilon C-O$ phenolic group is assigned to a band at 1145 cm^{-1}. The thiomide bands III and IV of free ligand are attributed to IR bands at 1232 and 940cm^{-1}.

Table 1 : IR spectral bands of ligand SalmtrH$_2$

Band Position	Assignments
3250 m	υOH
3115 a	υNH
3060 w	υCH Phenyl group

Continue of Table 1.........

2980 w	υCH side chain
1635 s	υCN+υC=C
1568 m	Phenyl ring skeletal
1536 s	δNH+thiomideI
1482 m ⌐	⌐ δNHring+phenylring
1445 vs	skeletal vibration
1342 s ⌐	└ thiomide band II
1320 w	δOH phenolic
1278 va	υC-N
1232 m	thiomide band III
1215 s	υC-C
1200 s	υN-N
1145 m	υC-O
1125 s ⌐	phenyl and
1050 s	triazole ring
1030 m	υC-C and υC-N
962 s ⌐	band
940 vs	thioamide band IV
820 s ⌐	phenyl ring (C-H) and.
805 vs	triazole ring (N-H) and
758 s	(C-H) out of plane
730 s ⌐	bending band
700 m ⌐	phenyl ring and

Continue of Table 1.........

660 a	triazole ring deformation
610 m	vibrations + thioamide
578 s	group deformation
540 w	vibrations
490 m	
465 m	
430 w	
375 w	
278 m	

W = weak ; m= medium; s= strong; vs = very strong

The υC=N frequency of [R$_2$Te(salmtr)], R$_2$Te(5-Me-salmtr)] and R$_2$Te(5-Ph-salmtr)] complex have shown bands at 1655-1632-1 cm^{-1} which was same asin their Schiff base ligand, suggesting noninvolument of nitrogen atom group of υC in coordination. But the υC=N frequency band in [R$_2$Te(salmtrH)$_2$], [R$_2$Te(5-Me-salmtrH)$_2$] and [R$_2$Te(5-Ph-salmtrH)$_2$] complexes have shown at 1620-1610 cm^{-1} which normally appeared at 1655-1632 cm^{-1} in their Schiff vase ligands, suggesting ivolument of υC=N group, nitrogen to the tellurium metal ion. The δ(OH) of free ligand is assigned to a band at 1320 cm^{-1}, disappeared in all these prepared complexes . The υC-O phenolic group is assigned to a band at 1145cm^{-1} which shifts to higher wave number and observed around 1350-1370cm^{-1}.

In [R$_2$Te (salmtr)], R$_2$Te (5 - Me (salmtr)] and [R$_2$Te (5 -Ph -salmtr)]

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complexes.

The thioamide bands which appear in free ligand attributed at 1232 and 940 cm^{-1} the former band shifts to higher wave number and latter move around 820-840 cm^{-1}. The major shift of thioamide band (which appear at 940 cm^{-1}) in the complexes is attributed to deprotonation of thiol SH and bonding of thioamede group through deprotonated thio sulphur atom of the ligand molecule. But in $[R_2Te(salmtrH)_2]$, $R_2Te(5\text{-}Te\text{-}salmtrH)_2]$ and $[R_2Te(5\text{-}Ph\text{-}salmtrH)_2]$ complexes the thioamide bands which appears at 1232 and 940 cm^{-1} in the free ligand have shown no change suggesting non-involvument of SH group in the complexation. In far IR υTe-C was observed 560-540 cm^{-1} in all these prepared complexes The υTe-X were absent in all these prepared complexes.

The X-ray photoelectron spectra data for $Te3d_{3.2\,,\,5.2}$, N1s, O1s and $2p$ are listed in table 3. It was noticed that $Te3d_{3.2\,,5.2}$ binding energy value decrease with respect to their R_2TeX_2; suggesting increase of electron density on tellurium metal ion due to coordination. (Fig 1 to 7).

In complexes $[R_2Te(salmtr)]$ $[R_2Te(5\text{-}Me\text{-}salmtr)]$ and $[R_2Te(5\text{-}ph\text{-}salmtr)]$ O_1s and $s2p$ binding energy values were observed more than their respective Schiff base ligand suggesting involument of oxygen and sulphur atom in the complexation . But during the analysis of N1s binding energy data, it was observed, no change in BE value with respect to their respective Schiff base ligand. Suggesting noninvolvement of nitrogen (of υC=N gp) in the complexation[8]. (Fig. 8)

During the study of [R$_2$Te(salmtrH)$_2$], [R$_2$Te(5-Me-salmtrH)$_2$], and [R$_2$Te(5-Ph-salmtrH)$_2$], it was observed that O1s and N1s binding energies values were increase with respect to their respective Schiff base lignd, while S2p binding energy values were observed same as in ligand. These observations concluded the involuement of nitrogen and oxygen atom, not sulphur atom in the complexation of these complexes (Fig 10).

Further it was noticed that all these prepared complexes have not shown X2p (X = Cl or I) photoelectron peak, suggesting their absence in the complexes.

On the badis of elemental analysis, molar conductivity IR and XPS data , the geometry of these complexes can be concluded and as shown in fig. i.e. trigonal bipyramidal in [R$_2$Te(Samtr)] and Pseudooctahedral in [R$_2$Te(SamtrH)$_2$] complexes.
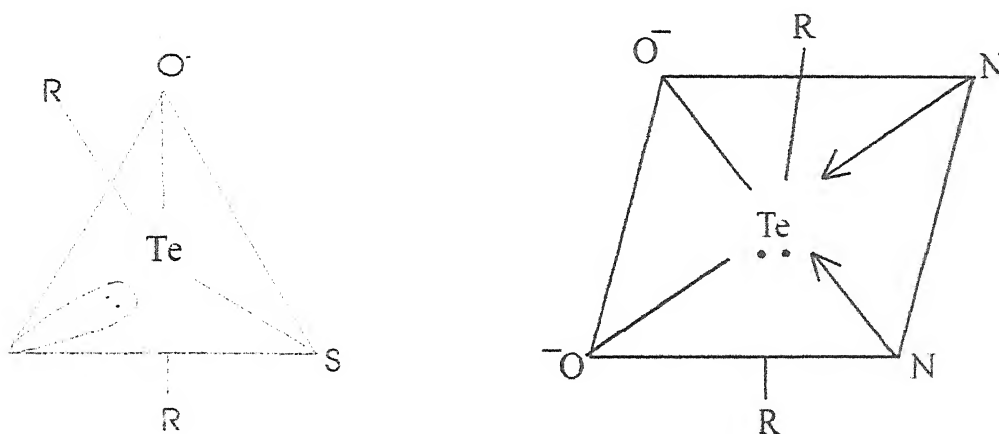
Geometry of [R$_2$Te(Samtr)] and [R$_2$Te.(SamtrH)]

(127)

Table-3 Te3d$_{3/2, 5/2}$; N1s, O1s and S2p binding energies(eV) in R$_2$TeX$_2$, [R$_2$Te(salmtr)$_2$] and [R$_2$Te(salmtrH)$_2$] complexes.

Sr.No.	Ligand and Complexes	Te metal ion		N1s	O1s	S2P
		Te3d$_{3/2}$	Te3d$_{5/2}$			
1.	SalmtrH$_2$	-	-	399.4	532.4	165.2
2.	5-Me- SalmtrH$_2$	-	-	399.4	532.4	165.2
3.	5-Ph- SalmtrH$_2$	-	-	399.4	532.4	165.2
4.	(C$_6$H$_5$CH$_2$)$_2$TeI$_2$	585.8	575.4	-	-	-
5.	[(C$_6$H$_5$CH$_2$)$_2$Te(Salmtr)]	584.2	574.2	-	534.6	166.4
6.	[(C$_6$H$_5$CH$_2$)$_2$Te(5MeSalmtr)]	584.2	574.2	-	534.6	166.4
7.	[(C$_6$H$_5$CH$_2$)$_2$Te(5Ph-Salmtr)]	584.2	574.2	-	534.6	166.4
8.	[(C$_6$H$_5$CH$_2$)$_2$Te(SalmtrH)$_2$]	584.2	574.2	402.8	534.6	-
9.	[(C$_6$H$_5$CH$_2$)$_2$Te(5Me-SalmtrH)$_2$]	584.2	574.2	402.8	534.6	-
10.	[(C$_6$H$_5$CH$_2$)$_2$Te(5Ph-SalmtrH)$_2$]	584.2	574.2	402.8	534.6	165.2
11.	[(C$_6$H$_4$)$_2$TeCl$_2$]	585.6	575.2	-	-	-
12.	[(C$_6$H$_4$)$_2$Te(Salmtr)]	584.2	574.0	399.4	534.6	166.4
13.	[(C$_6$H$_4$)$_2$Te(5Me-Salmtr)]	584.2	574.0	399.4	534.6	166.4
14.	[(C$_6$H$_4$)$_2$Te(5Ph-Salmtr)]	584.2	574.0	399.4	534.6	166.4
15.	[(C$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2

Continue of Table 3 ....

16.	[(C$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2
17.	[(C$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2
18.	[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$	585.6	575.6	-	-	-
19.	[(p-MeOC$_6$H$_4$)$_2$Te(Salmtr)]	584.2	574.0	399.4	534.6	166.4
20.	[(p-MeOC$_6$H$_4$)$_2$Te(5Me-Salmtr)]	584.2	574.0	399.4	534.6	166.4
21.	[(p-MeOC$_6$H$_4$)$_2$Te(5Ph-Salmtr)]	584.2	574.0	399.4	534.6	166.4
22.	[(p-MeOC$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2
23.	[(p-MeOC$_6$H$_4$)$_2$Te(5Me-SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2
24.	[(p-MeOC$_6$H$_4$)$_2$Te(5Ph-SalmtrH)$_2$]	584.2	574.0	402.6	534.6	165.2
25.	[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$TeCl$_2$]	585.6	575.6	-	-	-
26.	[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te(salmtr)]	584.4	574.2	399.4	534.6	166.4
27.	[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te(5Me-salmtr)]	584.4	574.2	399.4	534.6	166.4
28.	[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te(5Ph-salmtr)]	584.4	574.2	399.4	534.6 -	166.4
29.	[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(salmtrH)$_2$]	584.4	574.2	402.6	534.6	165.2
30.	[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(5Me-salmtrH)$_2$]	584.4	574.2	402.6	534.6	165.2
31.	[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(5Ph-salmtrH)$_2$]	584.4	574.2	402.6	534.6	165.2
32.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$]	585.8	575.4	-	-	-
33.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(salmtr)]	584.2	574.0	399.4	534.6	166.4
34.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5Me salmtr)]	584.2	574.0	399.4	534.6	166.4
35.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5Ph- salmtr)]	584.2	574.0	399.4	534.6	166.4

Continue of Table 3 ....

36.	[(*p*-Me₂NC₆H₄)(*p*-MeOC₆H₄)Te(salmtrH)₂]	584.2	574.0	402.8	534.6	165.2
37.	[(*p*-Me₂NC₆H₄)(*p*-MeOC₆H₄)Te(salmtrH)₂]	584.2	574.0	402.8	534.6	165.2
38.	[(*p*-Me₂NC₆H₄)(*p*-MeOC₆H₄)Te(salmtrH)₂]	584.2	574.0	402.8	534.6	165.2
39.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)TeCl₂]	585.4	575.6	-	-	-
40.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(salmtr)]	584.2	574.2	399.4	534.6	166.4
41.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(5Me salmtr)]	584.2	574.2	399.4	534.6	166.4
42.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(5Ph- salmtr)]	584.2	574.2	399.4	534.6	166.4
43.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(salmtrH)₂]	584.2	574.2	402.8	534.6	165.2
44.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(5Me salmtrH)₂]	584.2	574.2	402.8	534.6	165.2
45.	[(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)Te(5Ph-salmtrH)₂]	584.2	574.2	402.8	534.6	165.2
46.	(CH₃)₂TeI₂	585.6	575.8	-	-	-
47.	[(CH₃)₂Te(salmtr)]	584.2	574.2	399.4	534.6	166.4
48.	[(CH₃)₂Te(5Me salmtr)]	584.2	574.2	399.4	534.6 -	166.4
49.	[(CH₃)₂Te(5Ph-salmtr)]	584.2	574.2	399.4	534.6	166.4
50.	[(CH₃)₂Te(salmtrH)₂]	584.2	574.2	402.8	534.6	165.2
51.	[(CH₃)₂Te(5Me salmtrH)₂]	584.2	574.2	402.8	534.6	165.2
52.	[(CH₃)₂Te(5Ph-salmtrH)₂]	584.2	574.2	402.8	534.6	165.2

Table 2:- Elemental and molar conductivity data of [R$_2$Te(salmtr)] and [R$_2$Te(salmtrH)$_2$] complexes.

Sr. No.	Complexes	Te	C	H	N	Molar conductivity ohm^{-1} cm^2 mol^{-1}
1.	[(C$_6$H$_5$CH$_2$)$_2$Te(Salmtr)]	25.4 (25.6)	55.2 (55.4)	3.2 (3.6)	5.2 (5.6)	20
2.	[(C$_6$H$_4$)$_2$Te(Salmtr)]	27.0 (27.1)	53.4 (53.6)	2.8 (2.9)	5.8 (5.9)	22
3.	[(p -MeOC$_6$H$_4$)$_2$Te(Salmtr)]	25.4 (25.5)	55.0 (55.2)	4.2 (4.0)	5.6 (5.6)	24
4.	[(p -Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(salmtr)]	24.4 (24.8)	53.2 (53.6)	4.0 (4.0)	8.2 (8.1)	26
5.	[(p -Me$_2$NC$_6$H$_4$)(p -MeOC$_6$H$_4$)Te(salmtr)]	23.2 (23.4)	53.4 (53.8)	4.0 (4.2)	7.4 (7.7)	18
6.	[(p -Me$_2$NC$_6$H$_4$)(p -EtOC$_6$H$_4$)Te(salmtr)]	22.4 (22.8)	53.4 (53.7)	4.2 (4.2)	7.4 (7.5)	16
7.	[(CH$_3$)$_2$Te(salmtr)]	36.6 (36.7)	37.4 (37.9)	3.2 (3.4)	8.0 (8.0)	23

Continue of Table 2 ....

No.	Compound					
8.	[(C$_6$H$_5$CH$_2$)$_2$Te(5-Me Salmtr)]	24.8 (24.8)	56.2 (56.0)	4.2 (4.2)	5.4 (5.4)	24
9.	[(C$_6$H$_4$)$_2$Te(5-Me Salmtr)]	26.2 (26.4)	54.4 (54.6)	3.0 (3.3)	5.4 (5.8)	26
10.	[p-MeOC$_6$H$_4$)$_2$Te(5-Me Salmtr)]	24.1 (24.0)	54.2 (54.3)	4.0 (4.1)	5.0 (5.2)	28
11.	[p-MeNC$_6$H$_4$)C$_6$H$_5$Te(5-Me Salmtr)]	22.8 (22.9)	51.4 (51.7)	4.1 (4.1)	12.4 (12.5)	24
12.	[p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5Me Salmtr)]	22.4 (22.8)	53.6 (53.7)	4.2 (4.4)	7.2 (7.5)	20
13.	[p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(5Me-Salmtr)]	22.0 (22.2)	54.2 (54.4)	4.6 (4.7)	7.2 (7.3)	16
14.	[(CH$_3$)$_2$Te(5-Me-Salmtr)]	35.4 (35.8)	40.2 (40.4)	4.0 (3.9)	7.4 (7.8)	18
15.	[(C$_6$H$_5$CH$_2$)$_2$Te(5Ph-Salmtr)]	26.8 (26.8)	52.4 (52.1)	5.2 (5.0)	5.4 (5.8)	16
16.	[(C$_6$H$_4$)$_2$Te(5Ph-Salmtr)]	23.2 (23.4)	59.4 (59.4)	3.4 (3.2)	5.4 (5.1)	16
17.	[p-MeOC$_6$H$_4$)$_2$Te(5-Ph Salmtr)]	20.2 (20.0)	55.2 (55.4)	3.8 (3.8)	4.2 (4.4)	20

(132)

Continue of Table 2 ....

	Compound					
18.	[(p-MeNC$_6$H$_4$)C$_6$H$_5$Te(5-Ph SalmtrH)$_2$]	24.4 (24.2)	43.2 (43.2)	4.3 (4.7)	8.0 (7.9)	26
19.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5-Ph Salmtr)]	20.2 (20.5)	58.4 (58.0)	4.2 (4.3)	6.6 (6.7)	22
20.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(5-Ph salmtr)]	23.8 (23.8)	69.2 (69.5)	5.4 (5.4)	7.6 (7.8)	15
21.	[(CH$_3$)$_2$Te(5-Ph Salmtr)]	30.0 (30.1)	48.0 (48.1)	3.6 (3.8)	6.5 (6.6)	20
22.	[(C$_6$H$_5$CH$_2$)$_2$Te(SalmtrH)$_2$]	18.2 (18.4)	55.2 (55.5)	4.1 (4.0)	8.1 (8.0)	22
23.	[(C$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	19.2 (19.3)	54.2 (54.4)	3.2 (3.3)	8.2 (8.4)	24
24.	[(p-MeOC$_6$H$_4$)$_2$Te(SalmtrH)$_2$]	17.4 (17.6)	53.2 (53.0)	3.8 (3.9)	7.6 (7.7)	26 -
25.	[(p-MeOC$_6$H$_4$)(C$_6$H$_5$)Te(salmtrH)$_2$]	18.2 (18.0)	54.2 (54.3)	4.0 (4.1)	9.4 (9.9)	14
26.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(salmtrH)$_2$]	17.2 (17.3)	53.4 (53.8)	4.0 (4.2)	9.2 (9.5)	18
27.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(salmtrH)$_2$]	16.8 (16.9)	54.2 (54.4)	4.2 (4.4)	9.2 (9.3)	20

(133)

Continue of Table 2 ....

28.	[(CH$_3$)$_2$Te(salmtrH)$_2$]	23.4 (23.6)	44.2 (44.4)	3.6 (3.7)	10.2 (10.4)	22
29.	[(C$_6$H$_5$CH$_2$)$_2$Te(5-Me SalmtrH)$_2$]	17.6 (17.7)	56.4 (56.7)	4.2 (4.4)	7.6 (7.8)	12
30.	[(C$_6$H$_4$)$_2$Te(5-Me SalmtrH)$_2$]	18.2 (18.5)	55.6 (55.7)	3.6 (3.8)	8.0 (8.1)	10
31.	[(p-MeOC$_6$H$_4$)$_2$Te(5-Me SalmtrH)$_2$]	16.8 (16.9)	54.2 (54.3)	4.0 (4.2)	7.2 (7.4)	18
32.	[(p-MeOC$_6$H$_4$)C$_6$H$_5$Te(5-Me SalmtrH)$_2$]	17.0 (17.3)	55.2 (55.5)	4.8 (4.9)	9.4 (9.5)	16
33.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5-Me SalmtrH)$_2$]	16.4 (16.7)	54.4 (54.9)	4.2 (4.6)	9.0 (9.2)	14
34.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(5-Me SalmtrH)$_2$]	16.2 (16.4)	55.2 (55.5)	4.6 (4.8)	8.4 (8.9)	22
35.	[(CH$_3$)$_2$Te(5-Me SalmtrH)$_2$]	22.2 (22.4)	46.4 (46.5)	4.0 (4.2)	9.4 (9.8)	22
36.	[(C$_6$H$_5$CH$_2$)$_2$Te(5-Ph SalmtrH)$_2$]	15.0 (15.1)	62.4 (62.6)	4.0 (4.3)	6.3 (6.6)	24
37.	[(C$_6$H$_4$)$_2$Te(5-Ph SalmtrH)$_2$]	15.6 (15.7)	61.8 (61.9)	3.4 (3.6)	6.4 (6.8)	26

Continue of Table 2 ....

38.	[(p-MeOC$_6$H$_4$)$_2$Te(5-Ph SalmtrH)$_2$]	14.2 (14.6)	60.2 (60.3)	4.0 (4.1)	6.2 (6.4)	20
39.	[(p-MeOC$_6$H$_4$)C$_6$H$_5$Te(5-Ph SalmtrH)$_2$]	14.4 (14.9)	61.2 (61.5)	4.2 (4.3)	8.0 (8.2)	22
40.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5-Ph SalmtrH)$_2$]	14.2 (14.3)	60.2 (60.8)	4.1 (4.3)	7.6 (7.8)	24
41.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(5-Ph SalmtrH)$_2$]	14.0 (14.1)	61.0 (61.1)	4.4 (4.5)	7.2 (7.7)	28
42.	[(CH$_3$)$_2$Te(5-Ph SalmtrH)$_2$]	18.2 (18.4)	55.2 (55.5)	4.0 (4.0)	8.0 (8.0)	26

Te3d$_{3/2}$ photoelectron peak.

$[(C_6H_5CH_2)_2Te.(5Ph-SalmtrH)_2]$

$[(C_6H_5CH_2)_2Te.(5Me.SalmtrH)_2]$

$[(C_6H_5CH_2)_2Te.(SalmtrH)_2]$

$[(C_6H_5CH_2)_2Te.(5Ph-Salmtr)]$

$[(C_6H_5CH_2)_2Te.(5Me.Salmtr)]$

$[(C_6H_5CH_2)_2Te.(Salmtr)]$

$[(C_6H_5CH_2)_2Te.I_2$

578   584   BE(ev)   590   596
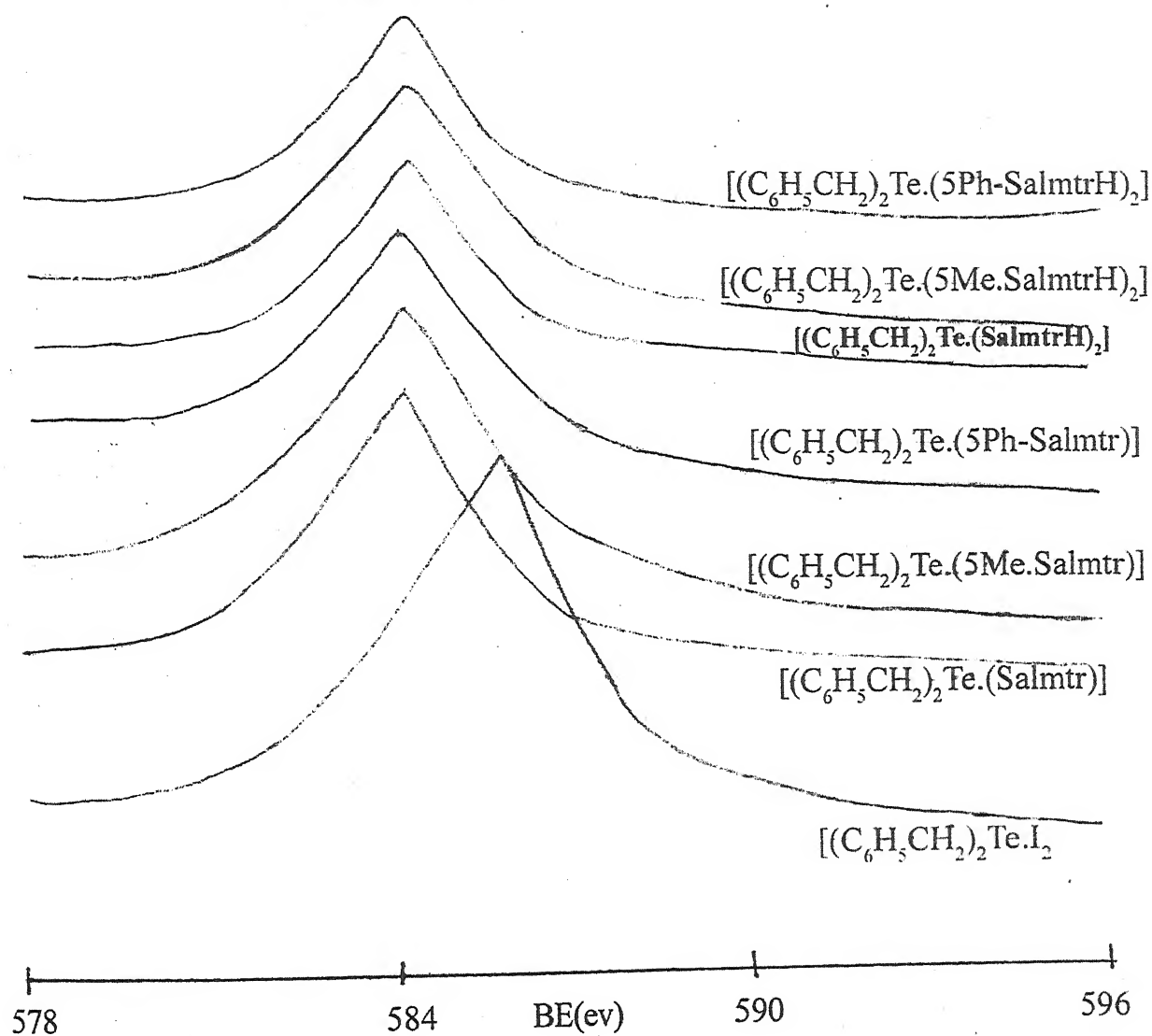
Fig 1 : Te 3d$_{3/2}$ binding energies (ev) in $(C_6H_5CH_2)_2$ Te I$_2$
$[(C_6H_5CH_2)_2Te(Salmtr)]$ and $[(C_6H_5CH_2)_2Te.(SalmtrH)_2]$

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Te3d$_{3/2}$ photoelectron peak.

$[(C_6H_4)_2Te.(5Ph-SalmtrH)_2]$

$[(C_6H_4)_2Te.(5Me-SalmtrH)_2]$

$[(C_6H_4)_2Te.(SalmtrH)_2]$

$[(C_6H_4)_2Te.(5Ph-Salmtr)]$

$[(C_6H_4)_2Te.(5Me-Salmtr)]$

$[(C_6H_4)_2Te.(Salmtr)]$

$[(C_6H_4)_2Te.Cl_2$

578   484   BE(ev)   590   596
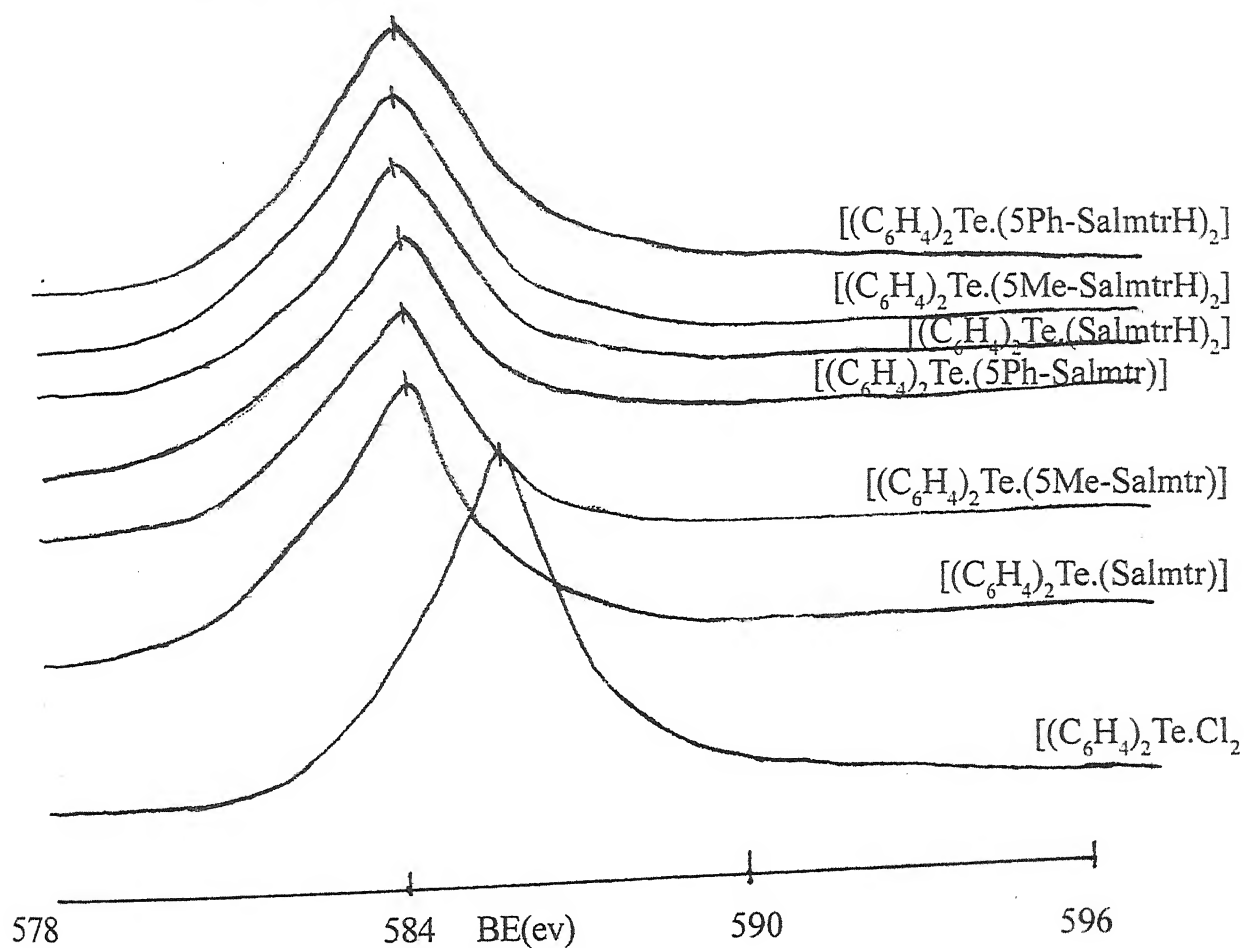
Fig 2 : Te 3d$_{3/2}$ binding energies (ev) in $(C_6H_4)_2$ Te Cl$_2$,
$[(C_6H_4)_2Te(Salmtr)]$ and $[(C_6H_4)_2Te.(SalmtrH)_2]$

Te3d$_{3/2}$ photoelectron peak.

[(p-MeOC$_6$H$_4$)$_2$Te.(5Ph-SalmtrH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te.(5Me-SalmtrH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te.(SalmtrH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te.(5Ph-Salmtr)]

[(p-MeOC$_6$H$_4$)$_2$Te.(5Me-Salmtr)]

[(p-MeOC$_6$H$_4$)$_2$Te.(Salmtr)]

[(p-MeOC$_6$H$_4$)$_2$Te.Cl$_2$

578   584   BE(ev)   590   596
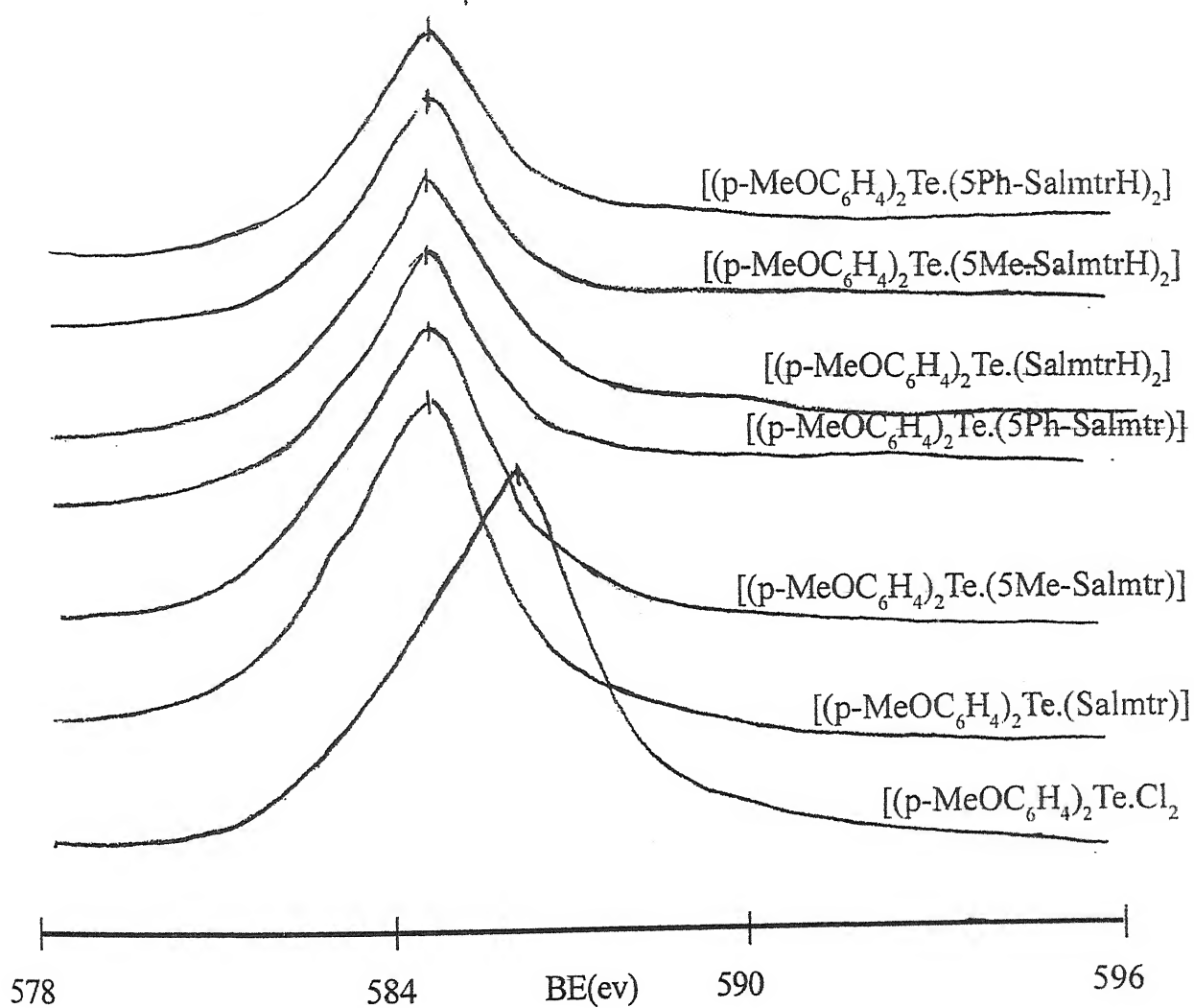
Fig 3 : Te 3d$_{3/2}$ binding energies (ev) in [(p-MeOC$_6$H$_4$)$_2$ Te Cl$_2$]
[(p-MeOC$_6$H$_4$)$_2$Te(Salmtr)] and [(p-MeOC$_6$H$_4$)$_2$Te.(SalmtrH)$_2$]

Te3d$_{3/2}$ photoelectron peak.

[(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te(5Ph-SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te.(5Me-SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te.(SalmtrH$_2$]

[(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te.(5Ph-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te.(5Me-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te.(Salmtr)]

[(p-Me$_2$NC$_6$H$_4$) C$_6$H$_5$Te.Cl$_2$]

578   584   BE(ev)   590   596
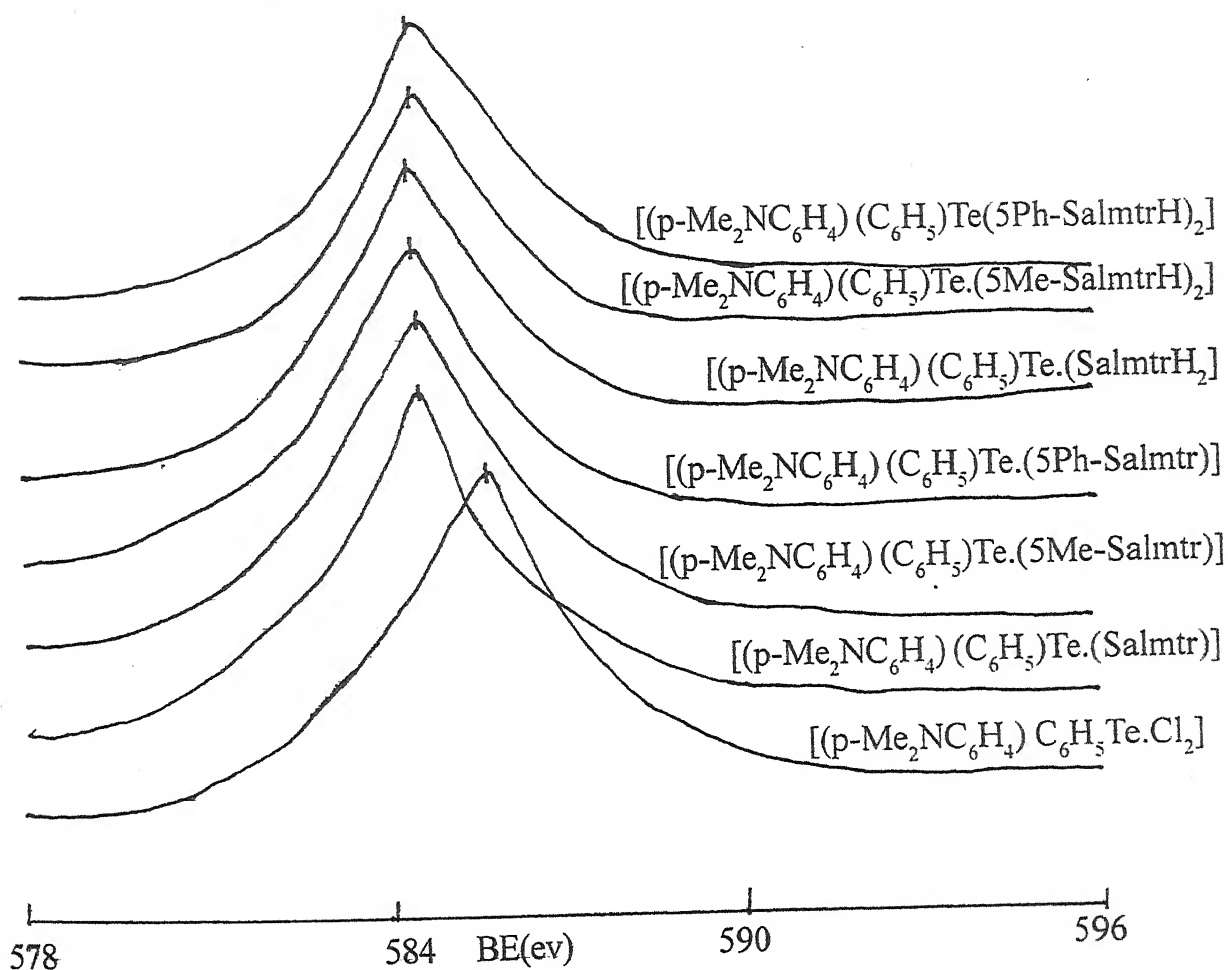
Fig 4 : Te 3d$_{3/2}$ binding energies (ev) in [(p-Me$_2$NC$_6$H$_4$) C$_6$H$_5$ Te Cl$_2$],
[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te(Salmtr)] and [(p-Me$_2$NC$_6$H$_4$) (C$_6$H$_5$)Te.(SalmtrH)$_2$]

Te3d$_{3/2}$ photoelectron peak.

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(5Ph-SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(5Me-SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(5Ph-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(5Me-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(Salmtr)]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.Cl$_2$]

578   584   BE(ev)   590   596
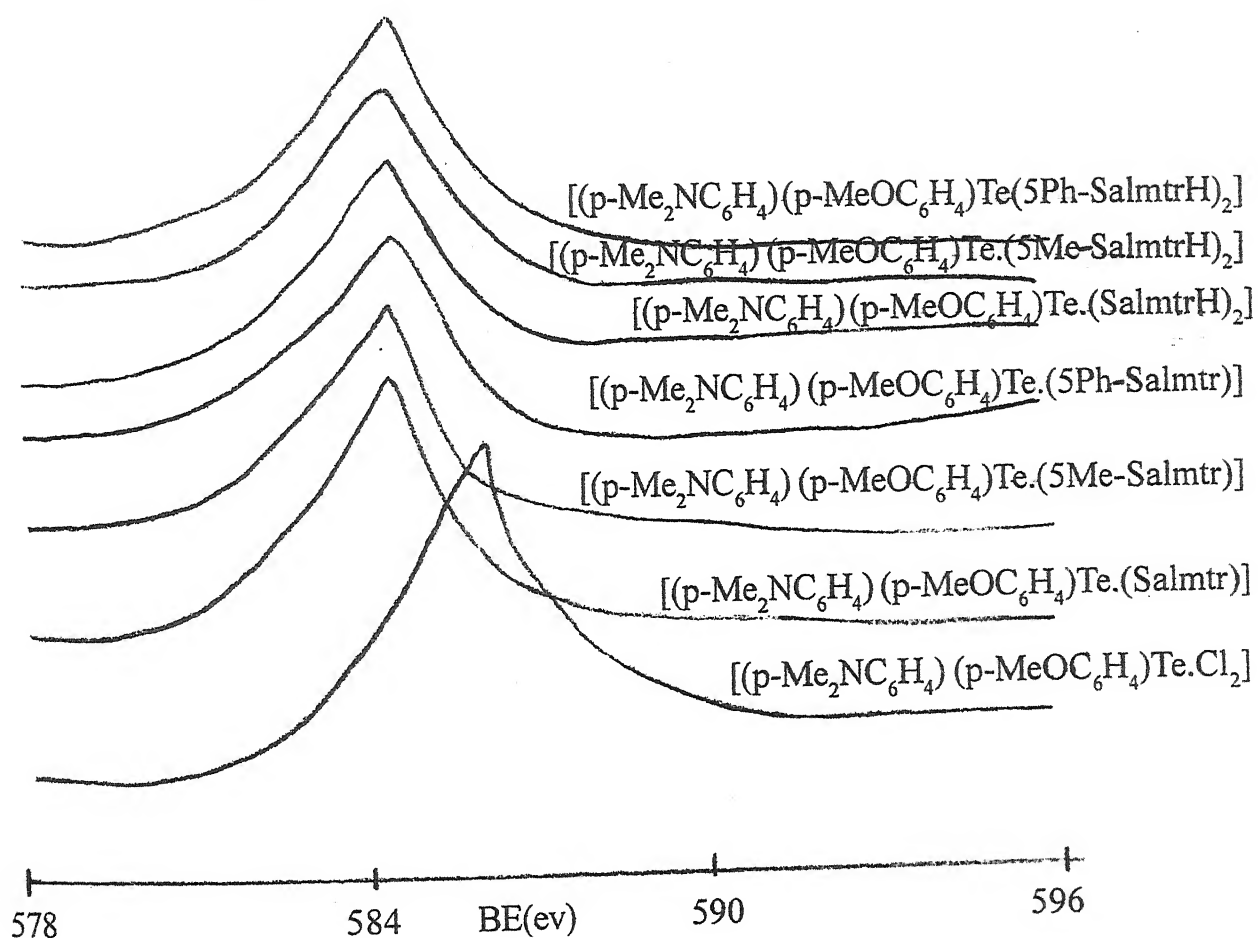
Fig 5 : Te 3d$_{3/2}$ binding energies (ev) in [(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$) Te Cl$_2$];
[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te(Salmtr)] and
[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)(SalmtrH)$_2$]

Te3d$_{3/2}$ photoelectron peak.

[(p-Me$_2$NC$_6$H$_4$) (p-EtOC$_6$H$_4$)
Te(5Ph-SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(5Me.SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(SalmtrH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(5Ph-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(5Me-Salmtr)]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(Salmtr)]

[(p-Me$_2$NC$_6$H$_4$) (p-EtOC$_6$H$_4$)TeCl$_2$

578   584   BE(ev)   590   596
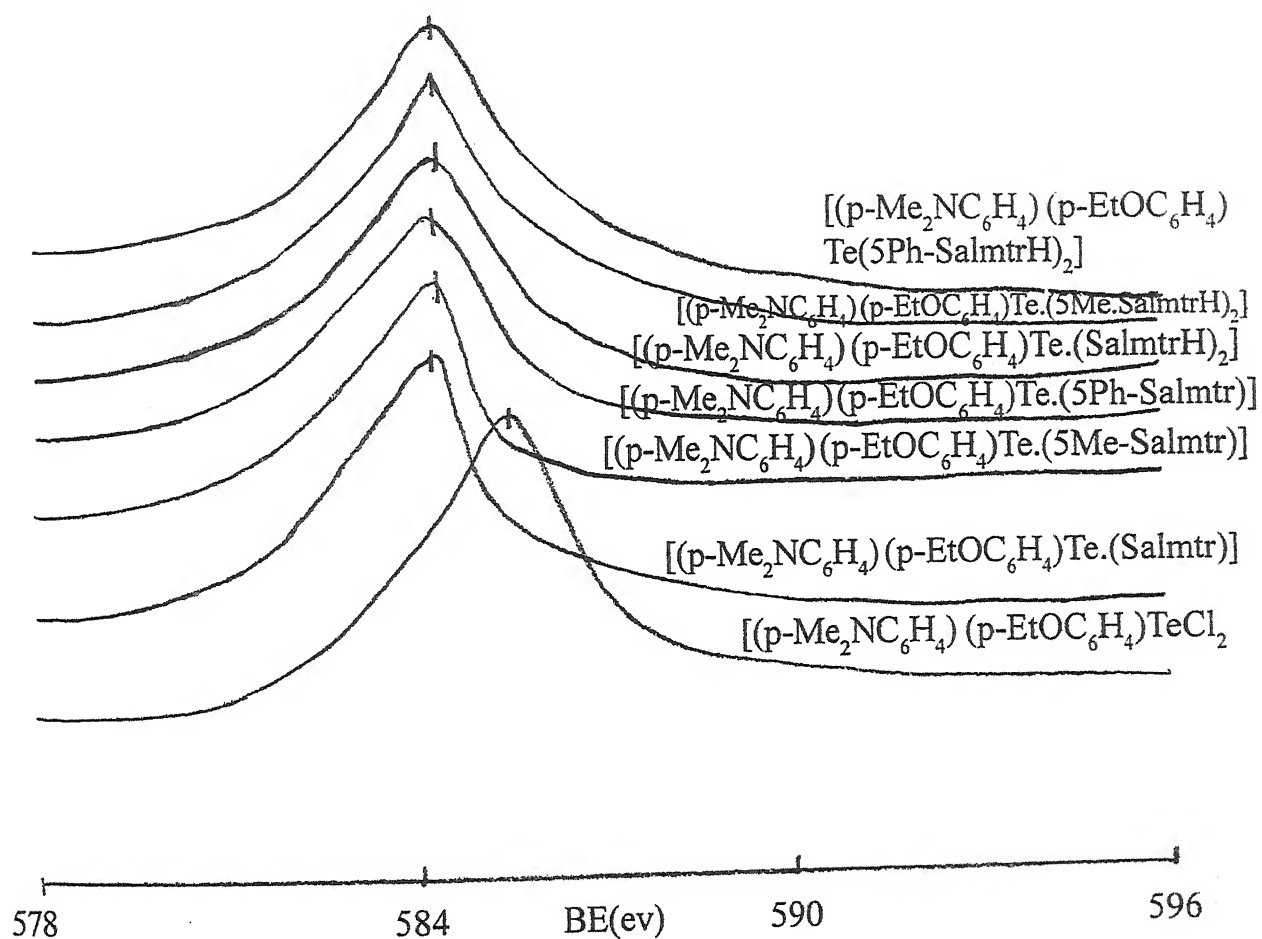
Fig 6 : Te 3d$_{3/2}$ binding energies (ev) in [(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$) Te Cl$_2$]
[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(Salmtr)]
and [(p-Me$_2$NC$_6$H$_4$) (p-EtOC$_6$H$_4$)Te.(SalmtrH)$_2$]

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Te3d$_{3/2}$ photoelectron peak.

[(CH$_3$)$_2$Te(5Ph-SalmtrH)$_2$]

[(CH$_3$)$_2$Te.(5Me-Salmtr)]

[(CH$_3$)$_2$Te.(SalmtrH)$_2$]

[(CH$_3$)$_2$Te.(5Ph-Salmtr)]

[(CH$_3$)$_2$Te.(5Me-Salmtr)]

[(CH$_3$)$_2$Te.(Salmtr)]

[(CH$_3$)$_2$Te.I$_2$

578   584   BE(ev)   590   596
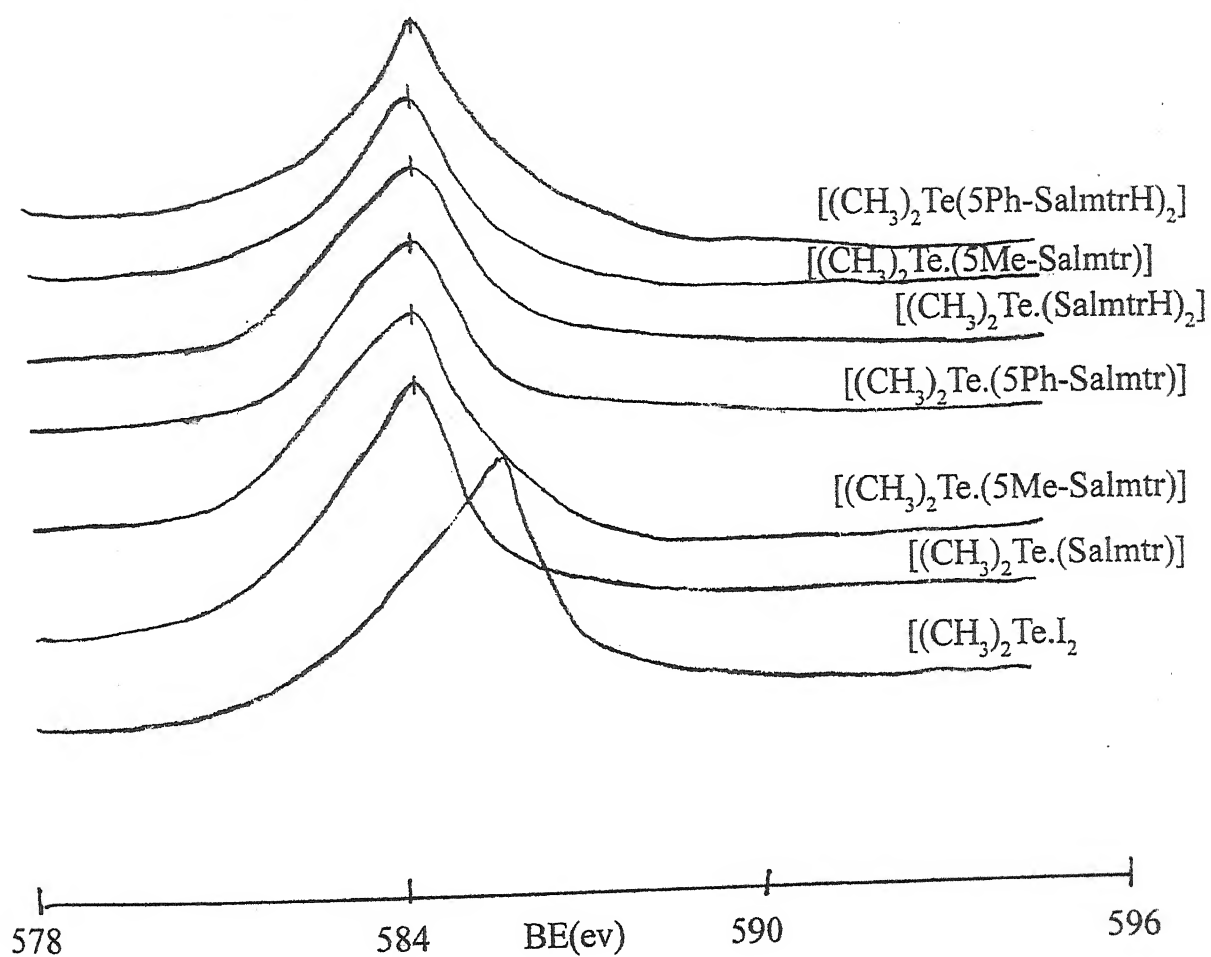
Fig 7 : Te 3d$_{3/2}$ binding energies (ev) in [(CH$_3$)$_2$ Te I$_2$];
[(CH$_3$)$_2$Te(Salmtr)] and [(CH$_3$)$_2$Te.(SalmtrH)$_2$]

N1s photoelectron peak
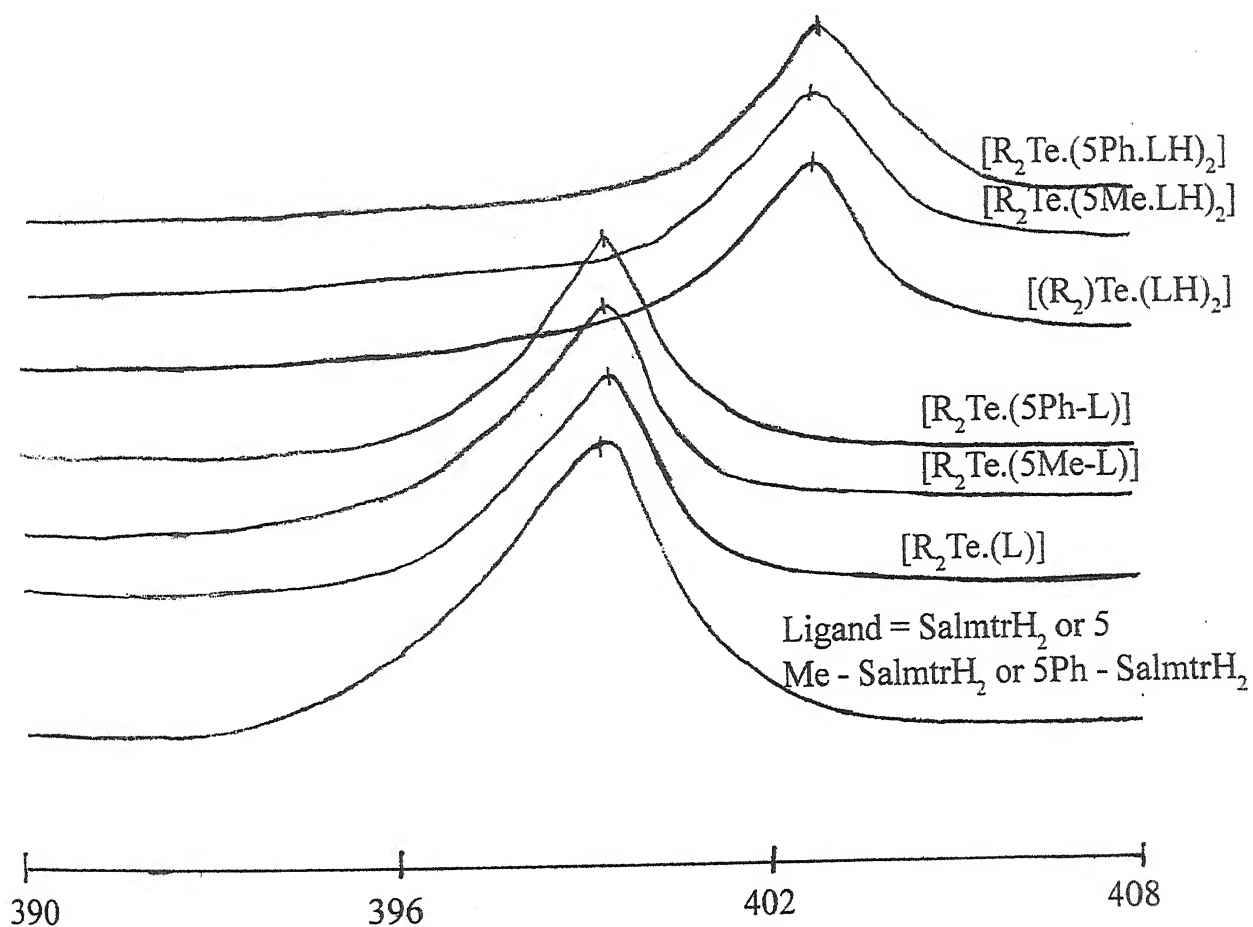
Fig 8 : N1s photoelectron peak in ligands, $[R_2Te.(L)]$
and $[(R_2)Te.(LH)_2]$ complexes

O1s photoelectron peak

[R$_2$Te.(5Ph-LH)$_2$]

[R$_2$Te.(5Me-LH)$_2$]

[R$_2$Te.(LH)$_2$]

[R$_2$Te.(5Ph-L)]

[R$_2$Te.(5Me-L)]

[R$_2$Te.(L)]

Ligand = SalmtrH$_2$ or
5Me - SalmtrH$_2$ or 5Ph - SalmtrH$_2$

524   530   536   542

BE(ev
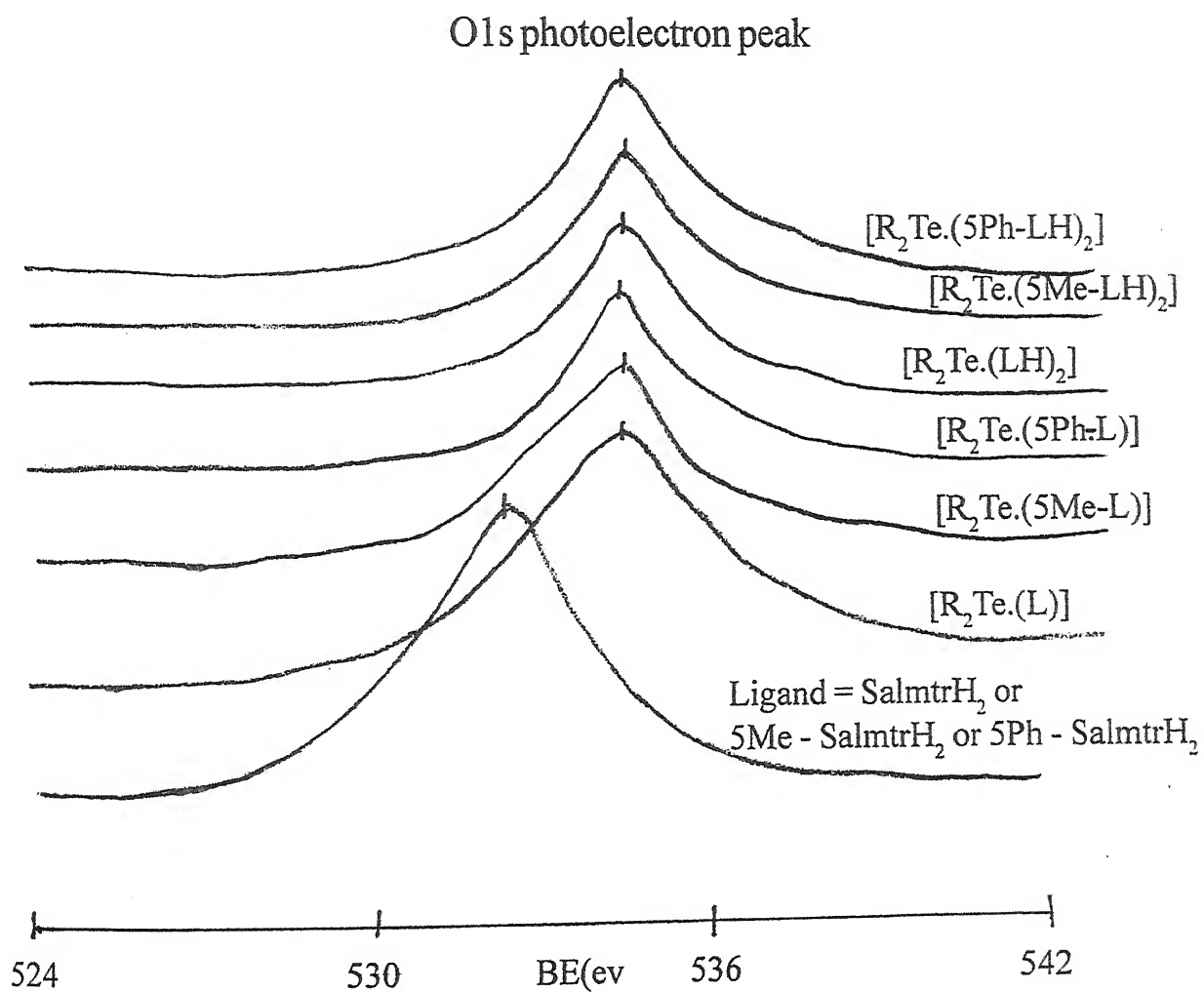
Fig 9 : O1s binding energies in Ligands [R$_2$Te.(L)] and [R$_2$Te.(LH)$_2$]

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S2p photoelectron peak

$[R_2Te.(5Ph.LH)_2]$

$[R_2Te.(5Me-LH)_2]$

$[R_2Te.(LH)_2]$

$[R_2Te.(5Ph.L)]$

$[R_2Te.(5Me-L)]$

$[R_2Te.(L)]$

Ligand = $SalmtrH_2$ or $5Me - SalmtrH_2$ or $5Ph - SalmtrH_2$

158   164   BE(ev)   170   176
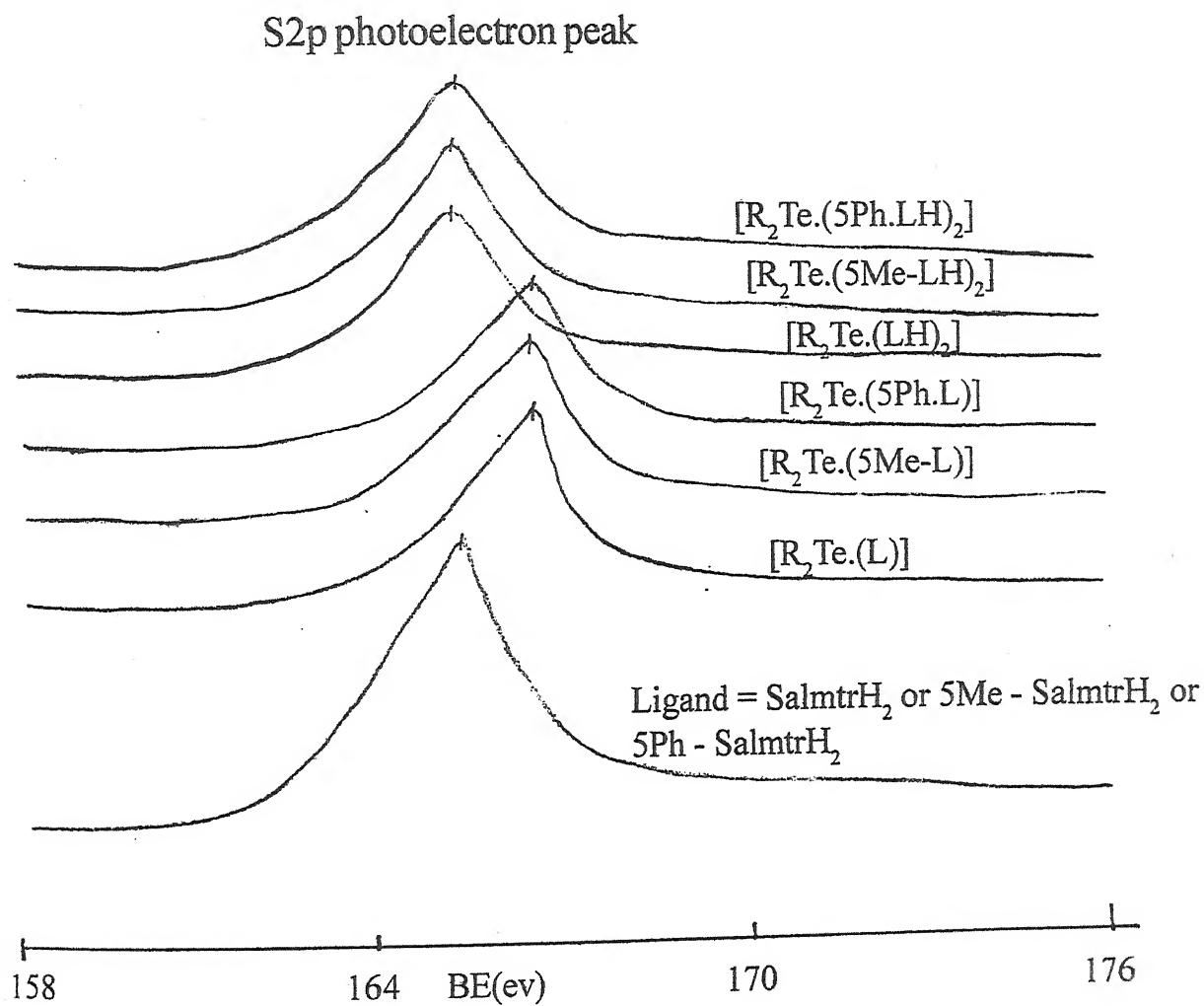
Fig 10 : S2p binding energies (ev) in Ligands; $[R_2Te.(L)]$
and $[R_2Te.(LH)_2]$ complexes

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CHAPTER IV

COMPLEXES OF R$_2$TeX$_2$ WITH 3-MERCAPTO-4-β-ISATINYLIMINO-1,2,4-TRIAZOLE

"COMPLEXES OF R₂TeX₂ WITH 3-MERCAPTO-4-β-ISATINYLIMINO-1,2,4-TRIAZOLE"

4-amino-3-mercapto-1,2,4-triazole(mtrH) readily condenses with isatine in hot methanol giving 3-mercapto-4-β-isatainylimino-1,2,4-triazole(IstmtrH).
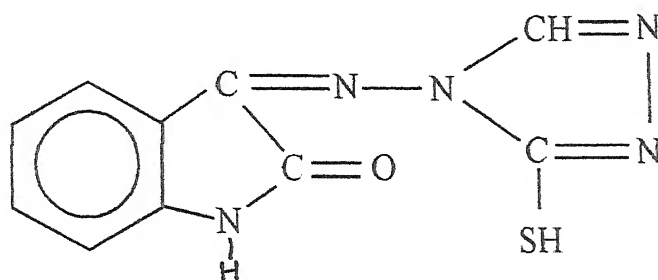
Structure of (Ist mtrH)

The consedered Schiff Base (IstmtrH) contains several donor sites, four nitro, one sulphur and one oxygen.

EXPERIMENTAL

Preparation of [R₂TeX₂(IstmtrH)]

The R_2TeX_2(1mmol) i.e. $(C_6H_5CH_2)_2TeI_2$; $(C_6H_4)_2TeCl_2$; $(p\text{-}MeOC_6H_4)_2TeCl_2$; $(p\text{-}Me_2N.C_6H_4)$ $PhTeCl_2$; $(p\text{-}Me_2NC_6H_4)$ $(p\text{-}MeOC_6H_4)TeCl_2$; $[(p\text{-}Me_2NC_6H_4)$ $(p\text{-}EtOC_6H_4)TeCl_2]$ and $(CH_3)_2TeI_2$. was dissolved in CH_3OH with istmtrH ligand (1 mmol) and refluxed for 2-3 hrs. The solid product obtained after rotary evaporation was purified by pet. Ether(b.p. 60-80⁰), air-dried and kept in desiccators.

Preparation of [R₂Te(Istmtr)₂]

The R_2TeX_2(1mmol) i.e. $(C_6H_5CH_2)_2TeI_2$; $(C_6H_4)_2TeCl_2$; $(p\text{-}MeOC_6H_4)_2TeCl_2$; $(p\text{-}Me_2N.C_6H_4)$ $PhTeCl_2$; $(p\text{-}Me_2NC_6H_4)$ $(p\text{-}MeOC_6H_4)TeCl_2$; $[(p\text{-}Me_2NC_6H_4)$ $(p\text{-}EtOC_6H_4)TeCl_2]$ and $(CH_3)_2TeI_2$. was dissolved in CH_3OH with istmtrH ligand (2 mmol) and refluxed for 3 hrs. The solid product obtained after rotary evaporation was purified by pet. Ether(b.p. 60-80⁰), air-dried and kept in desiccators.

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Results and Discussions

The results of elemental analysis and molar conductivity of [R_2TeX_2.(IstmtrH)] and [$R_2Te.(Ismtr)_2$] complexes are listed in table 1. The complexes are quite stable in air and partially soluble in mthanol, ethanol, di-oxin, DMF and DMSO. The DMF solutions of complexes at room temperature display negligible electrical conductance value indicating their non-ionic nature[1].

IR data of ligand (IstmtrH) are listed in table 2. The prepared [R_2TeX_2.(IstmtrH)] complexes and [R_2TeX_2.(Istmtr)$_2$] complexes exhibited $\upsilon_{C=N}$ band at around 1620 – 1610 cm^{-1}. The lowering of this band in the complexes indicates the coordination of nitrogen atoms of azomethine groups to the tellurium metal ion the far IR for Te-N^2 and υ_{Te-C}^2 appeared at 420-410, and 560-540 cm-1 respectively. But υTe-X were absent in [$R_2Te(Ismtr)_2$] complexes. The $\upsilon_{C=O}$ band(isatinic ketone) in [R_2TeX_2.(IsmtrH)] complexes at 1720-1740, which normally appeared in ligand at 1760-1732 cm-1. The lowereing of $\upsilon_{C=O}$ in the complexes also indicate the coordination of oxygen atom of isatinic ketone with tellurium metal ion. But the position of $\upsilon_{C=O}$ in [$R_2(Te.1stmtr)_2$] complexes does not change with respect ot ligand. This indicate the non-coordination of oxygen of isatinic ketone with tellurium metal ion in these complexes. The thioamide band I, and II and III were observed in the ligand at 1498 cm-1, 1375 and 1208 cm-1, which is observed to appear on the same positon in these [R_2TeX_2.(IstmtrH)] tellurium metal complexes, suggesting non-involvement of thioamide group. But the frequency position of thioamide band I, II and III is observed to raised to higher frequencies in [$R_2Te(Istmtr)_2$] complexes which are taken to be taken characteristic of coordinated thioamide group.

It was observed that the binding energy fo Te3d$_{3/2}$, $_{5/2}$ in the starting material R_2TeX_2 was higher than their prepared complexes table 3. This observation concludes that electron density on Te metal ion has been increased by coordination of Schiff base ligands with tellurium metal ion[3]. (Fig. 1 & 2)

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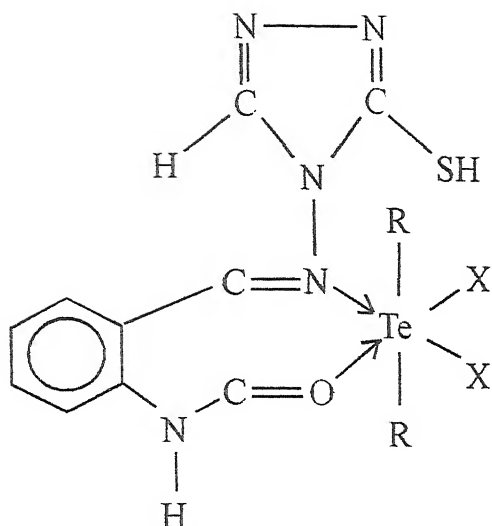
Structure of [R₂TeX₂(IstmtrH)] complexes
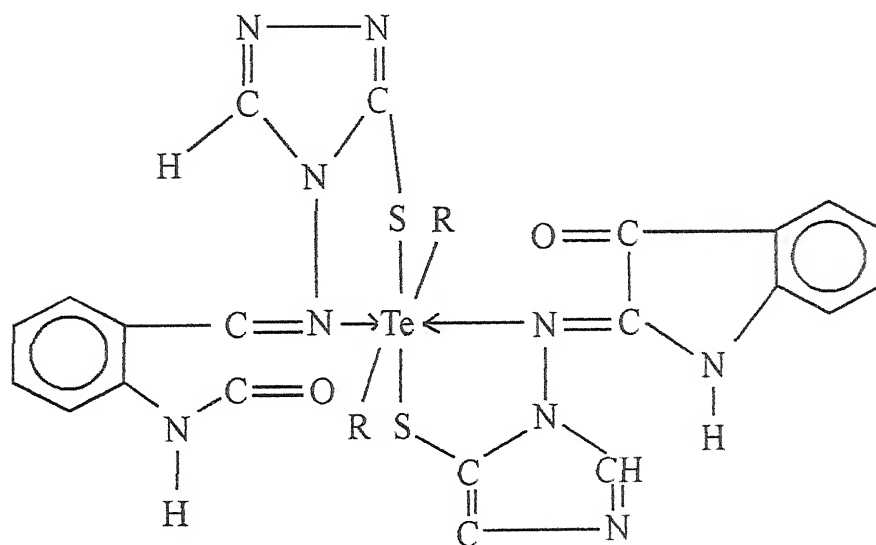
Structure of [R₂Te(Istmtr)₂] complexes

It was observed that N1s binding energies of C=N group were higher in all these prepared complexes than the ligands; suggesting ivolvemetn of nitrogen atom in the coordintation. It was noticed that O1s binding energy in [R₂TeX₂.(IstmtrH)] complexes were higher than O1s binding energy of ligand suggesting involvement of oxygen atom in coordination but O1s binding

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energy were same in the ligand and $[R_2Te(Istmtr)_2]$ complexes, suggesting non-involvement of oxygen atom in coordination in $[R_2Te.(Istmtr)_2]$ complexes[3] Fig.3 and 4. Morever, $S2p_{3/2}$ photoelectron peak have shown same binding energy data in $[R_2TeX_2.(IstmtrH)]$ complexes as in ligand suggesting non involvement of sulphur atom in coordination in these $[R_2Te(Istmtr)_2]$ complexes[3] but in $[R_2Te(Istmtr)_2]$ complexes photoelectron binding energy is increased than the ligand , suggesting involvement of sulphur atom in coordination in these complexes i.e. in $[R_2Te.(Istmtr)_2]$ complexes[3] Fig5 and 6.

On the basis of elemental analysis, conductivity results showing the all the complexes to be non-ionic and IR and X-Ray photoelectron(XPS) identifying the site of coordintation it is possible to conclude that all these prepared complexes have pseudoctahedral geometry as show in fig 7(a) and 7(b).

Geometry of $[R_2TeX_2(IstmtrH)]$
complexes

(a)

Geometry of $[R_2Te(Istmtr)_2]$
complexes

(b)
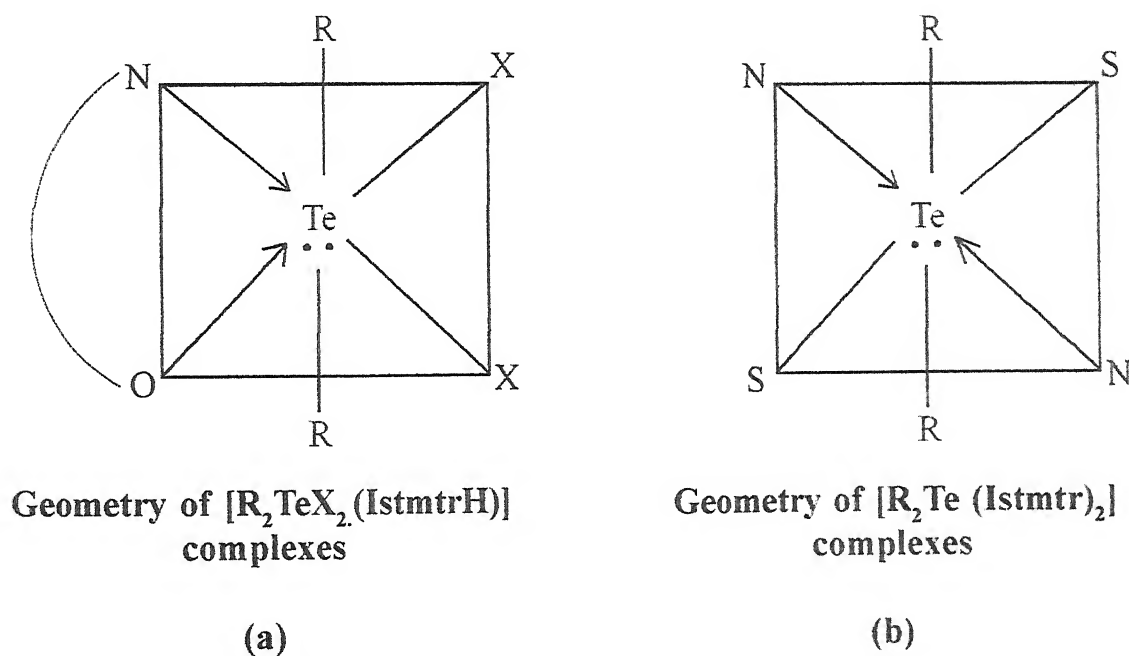
Fig. 7

Table 1:- Elemental analysis and molar conductivity values for the compounds

Sr. No	Compound	Found (Calc.)(%)				Molar conductivity (ohm−1 cm² mol⁻¹)
		Te	C	H	N	
1.	[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$.(IstmtrH)]	12.2 (12.0)	27.0 (27.1)	1.8 (1.9)	6.4 (6.6)	10
2.	[(C$_6$H$_4$)$_2$TeCl$_2$.(IstmtrH)]	44.2 (44.3)	21.2 (21.4)	2.4 (2.5)	28.4 (28.5)	15
3.	[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$.(IstmtrH)]	19.4 (19.8)	44.6 (44.8)	3.0 (3.2)	10.8 (10.9)	20
4.	[(p-Me$_2$NC$_6$H$_4$)$_2$PhTeCl$_2$(IstlmtrH)]	14.2 (14.4)	32.4 (32.5)	2.4 (2.5)	9.4 (9.5)	22
5.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$(IsmtrH)]	18.8 (18.9)	45.0 (45.2)	3.4 (3.5)	12.0 (12.4)	24
6.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$(IsmtrH)]	18.4 (18.6)	45.2 (45.6)	2.0 (2.3)	12.0 (12.2)	26
7.	(CH$_3$)$_2$TeI$_2$. (IsmtrH)]	0.1 (0.1)	15.4 (15.8)	1.4 (1.4)	7.6 (7.7)	28

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Continue of Table 1 ....

8.	[(C₆H₅CH₂)₂Te. (Ismtr)₂]	15.8 (15.9)	51.2 (51.4)	3.2 (3.3)	17.4 (17.5)	26
9.	[(C₆H₄)₂Te. (Ismtr)₂]	16.8 (16.6)	50.2 (50.0)	2.4 (2.6)	18.0 (18.2)	24
10.	[(p -MeOC₆H₄)₂Te(Ismtr)₂]	15.4 (15.6)	50.5 (50.8)	3.0 (3.1)	17.0 (17.2)	22
11.	[(p -Me₂NC₆H₄)₂ Ph Te.(Ismtr)₂]	15.4 (15.7)	50.0 (50.2)	3.3 (3.3)	18.8 (18.9)	20
12.	[(p -Me₂NC₆H₄) (p -MeOC₆H₄)₂ Te.(Ismtr)₂]	15.0 (15.1)	49.6 (49.8)	3.2 (3.4)	18.2 (18.3)	26
13.	[(p -Me₂NC₆H₄) (p -EtOC₆H₄)₂ Te.(Ismtr)₂]	14.8 (14.9)	50.2 (50.4)	3.4 (3.6)	17.8 (17.9)	22
14.	[(CH₃)₂Te.(Ismtr)₂]	19.6 (19.8)	40.6 (40.8)	2.6 (2.8)	21.6 (21.7)	14

Table 2:- IR of Ligand (IstmtrH)

Band Position	Assignments
3220-3100 abr	NH stretching band
2950 wbr	C-H stretching band
2840-2800 wbr	
1820 wbr	Over tone band
1760 wbr	$V_{C=O}$ isatanic ketone
1732 vsbr	
1655-1632 vsbr	Azomethyl $(C=N) + V_{C=C}$
1498 s	Thioamide band I
1440 sbr	Phenyl ring skeletal band
1375 mbr	Thioamide band II
1350 W	δ NH
1325 wbr	V_{C-N} of triazole + V_{C-N} of side chain

(153)

Continue of Table 2 ....

1270 s	
1240 wbr	Thioamide band III
1208 s	Phenyl and triazole
1170 wbr	
1105 m	Ring different mode of vibrations
1062 mbr	
1015 mbr	$\nu_{c-N}, \nu_{c-C}, \nu_{N-N}$
970 m	C-H and N-H out of plane bending band.
945 m	Thioamide band IV
852 mbr	C-H and N-H out of plane bending band.
760-755 sbr	
705	
660 mbr	Triazole and isatine part ring deformation vibrations.

Continue of Table 2 ....

615-600 mbr	
560 wbr	
362 wbr	

W = weak, wbr = weak and board, m= medium, mbr = medium and board; s = strong, sbr = strong and broad, vsbr = very strong and broad

Table 3:- $Te3d_{3/2, 5/2}$, N1s, O1s and S2p binding energies (ev) in ligand (IstmtrH), $[R_2TeX_2.(IstmtrH)]$ and $[R_2Te.(Istmtr)_2]$ complexes

Sr. No.	Compound	Metal Ion		N1s(for ligand nitrogen only)	O1s for ligand Oxygen	S2p
		$Te3d_{3/2}$	$Te3d_{5/2}$			
1.	Ligand(IsmtrH)	-	-	400.2	533.2	165.2
2.	$(C_6H_5CH_2)_2TeI_2$	585.8	575.4	-	-	-
3.	$[(C_6H_5CH_2)_2TeI_2.(IstmtrH)]$	584.0	574.0	402.8	534.8	165.2
4.	$[(C_6H_5CH_2)_2Te.(Ismtr)_2]$	584.0	574.0	402.8	532.2	166.0
5.	$(C_6H_4)_2TeCl_2$	585.6	575.2	-	-	-
6.	$[(C_6H_4)_2TeCl_2.(IstmtrH)]$	584.4	574.0	402.8	534.6	165.2
7.	$[(C_6H_5)_2Te.(Ismtr)_2]$	584.4	574.0	402.8	533.2	166.0
8.	$[(p-MeOC_6H_4)_2TeCl_2]$	585.8	575.4	-	-	-
9.	$[(p-MeOC_6H_4)_2TeCl_2.(IstmtrH)]$	584.6	574.2	402.6	534.6	165.2
10.	$[(p-MeOC_6H_4)_2Te(Ismtr)_2]$	584.6	574.2	402.6	533.2	166.0
11.	$(p-MeNC_6H_4)PhTeCl_2$	585.6	575.6	-	-	-
12.	$[(p-MeNC_6H_4)_2PhTeCl_2.(IstmtrH)]$	584.2	574.2	402.6	534.8	165.2
13.	$[(p-MeNC_6H_4)_2Ph Te.(Ismtr)_2]$	584.2	574.2	402.6	533.2	166.0
14.	$[(p-MeNC_6H_4)(p-MeOC_6H_4)TeCl_2$	585.8	575.4	-	-	-

Continue of Table 3 ....

No.	Compound					
15.	[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$(IsmtrH)]	584.4	574.2	402.6	534.8	165.2
16.	[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$) Te.(Ismtr)$_2$]	584.4	574.2	402.6	533.2	166.0
17.	[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$) TeCl$_2$	585.4	575.6	-	-	-
18.	[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$(IsmtrH)]	584.2	584.2	402.8	534.8	165.2
19.	[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$) Te.(Ismtr)$_2$]	584.2	584.2	402.8	533.2	166.0
20.	(CH$_3$)$_2$TeI$_2$	585.6	575.8	-	-	-
21.	(CH$_3$)$_2$TeI$_2$.(IsmtrH)	584.2	584.2	402.6	534.8	165.2
22.	[(CH$_3$)$_2$Te.(Istmtr)$_2$]	584.2	584.2	402.6	533.2	166.0

Te3d$_{3/2}$ photoelectron spectra.

[(CH$_3$)$_2$Te.(Istmtr)$_2$]

[(CH$_3$)$_2$TeI$_2$.(IstmtrH)]

[(CH$_3$)$_2$TeI$_2$]

[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$.(IstmtrH)]

[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$]

[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$(IstmtrH)]

[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$]

578   584   BE(ev)   590   596

Fig 1 : Te 3d$_{3/2}$ binding energies (ev) in [R$_2$TeX$_2$]; [R$_2$TeX$_2$(IstmtrH)]
and [R$_2$Te.(Istmtr)$_2$] complexes

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Te3d$_{3/2}$ photoelectron peak.

[(p-MeNC$_6$H$_4$)PhTe.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)PhTeCl$_2$.(IstmtrH)]

[(p-MeNC$_6$H$_4$)PhTeCl$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$.(IstmtrH)]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$]

[(C$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[(C$_6$H$_4$)$_2$TeCl$_2$]

[(C$_6$H$_5$CH$_2$)$_2$Te(Istmtr)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$(IstmtrH)]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$]

578   584   BE(ev)   590   596

Fig 2 : Te 3d$_{3/2}$ binding energies (ev) in [R$_2$TeX$_2$]; [R$_2$TeX$_2$(IstmtrH)]
and [R$_2$Te.(Istmtr)$_2$] complexes

N1s photoelectron spectra

[(p-MeNC$_6$H$_4$)PhTe.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)PhTeCl$_2$(IstmtrH)]

[Ligand (IstmtrH)]

[(p-MeOC$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[Ligand (IstmtrH)]

[(C$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[Ligand (IstmtrH)]

[(C$_6$H$_5$CH$_2$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$(IstmtrH)]

[(IstmtrH) = Ligand]

392   398   BE(ev)   404   410

Fig 3 : N1s binding energies (ev) in (IstmtrH) Ligand, [R$_2$TeX$_2$(IstmtrH)] and [R$_2$Te.(IstmtrH)$_2$] complexes

N1s photoelectron spectra
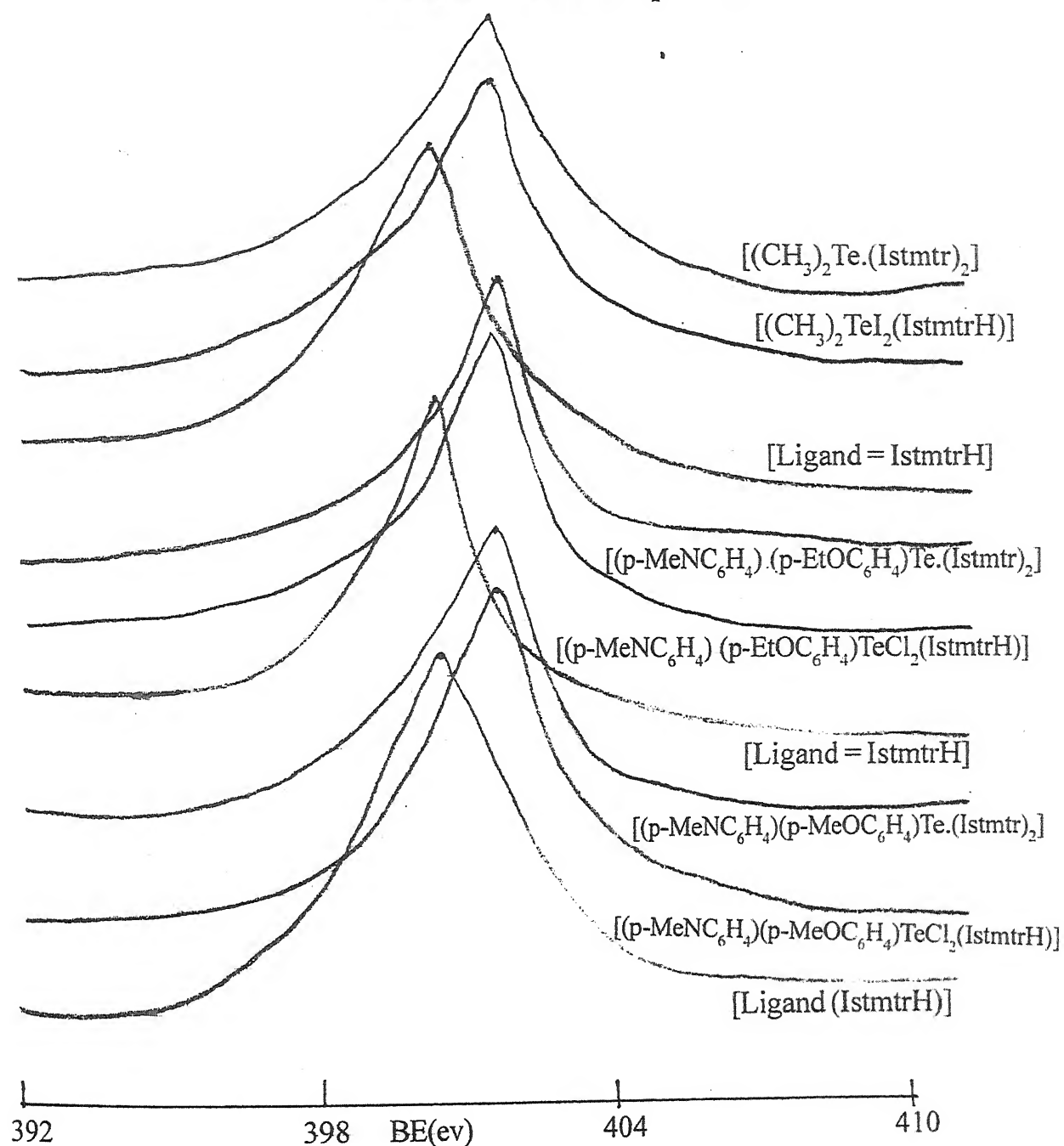
$[(CH_3)_2Te.(Istmtr)_2]$

$[(CH_3)_2TeI_2(IstmtrH)]$

[Ligand = IstmtrH]

$[(p\text{-}MeNC_6H_4).(p\text{-}EtOC_6H_4)Te.(Istmtr)_2]$

$[(p\text{-}MeNC_6H_4)(p\text{-}EtOC_6H_4)TeCl_2(IstmtrH)]$

[Ligand = IstmtrH]

$[(p\text{-}MeNC_6H_4)(p\text{-}MeOC_6H_4)Te.(Istmtr)_2]$

$[(p\text{-}MeNC_6H_4)(p\text{-}MeOC_6H_4)TeCl_2(IstmtrH)]$

[Ligand (IstmtrH)]

392   398   BE(ev)   404   410

Fig 4 : N1s binding energies (ev) in   (IstmtrH) Ligand, $[R_2TeX_2(IstmtrH)]$
and $[R_2Te.(Istmtr)_2]$ complexes

O1s photoelectron spectra

Fig 5 : O1s binding energies (ev) in Ligand, (IstmtrH)
[R_2TeX_2.(IstmtrH)] and[R_2Te.(Istmtr)$_2$] complexes

O1s photoelectron peak

[(p-MeNC$_6$H$_4$)PhTe(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)PhTeCl$_2$(IstmtrH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te(Istmtr)$_2$]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[(C$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[(C$_6$H$_5$CH$_2$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$(IstmtrH)]

[(IstmtrH = Ligand]

525   531   BE(ev)   537   543

Fig 6 : O1s binding energies (ev) in Ligand, (IstmtrH), [R$_2$TeX$_2$(IstmtrH)]

and [R$_2$Te.(Istmtr)$_2$] complexes

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S2p photoelectron spectra.

[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)(p-MeOC$_6$H$_4$)TeCl$_2$(IstmtrH)]

[(p-MeNC$_6$H$_4$)PhTe(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)PhTeCl$_2$(IstmtrH)]

[(p-MeOC$_6$H$_4$)$_2$Te(Istmtr)$_2$]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[(C$_6$H$_4$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_4$)$_2$TeCl$_2$(IstmtrH)]

[(C$_6$H$_5$CH$_2$)$_2$Te.(Istmtr)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$(IstmtrH)]

[(IstmtrH) Ligand]

158   164   BE(ev)   170   176

Fig 7(a) : S2p binding energies (ev) in Ligand, [R$_2$TeX$_2$(IstmtrH)]
and [R$_2$Te.(Istmtr)$_2$] complexes

S2p photoelectron Spectra.

[(CH$_3$)$_2$Te.(Istmtr)$_2$]

[(CH$_3$)$_2$TeI$_2$(IstmtrH)]

[(p-MeNC$_6$H$_4$)(pEtOC$_6$H$_4$)Te.(Istmtr)$_2$]

[(p-MeNC$_6$H$_4$)(pEtOC$_6$H$_4$)TeCl$_2$(IstmrH)]

[Ligand (IstmtmH)]

158   164   BE(ev)   170   176

Fig 7(b) : S2p binding energies (ev) in ligand, [R$_2$TeX$_2$(IstmtrH)]
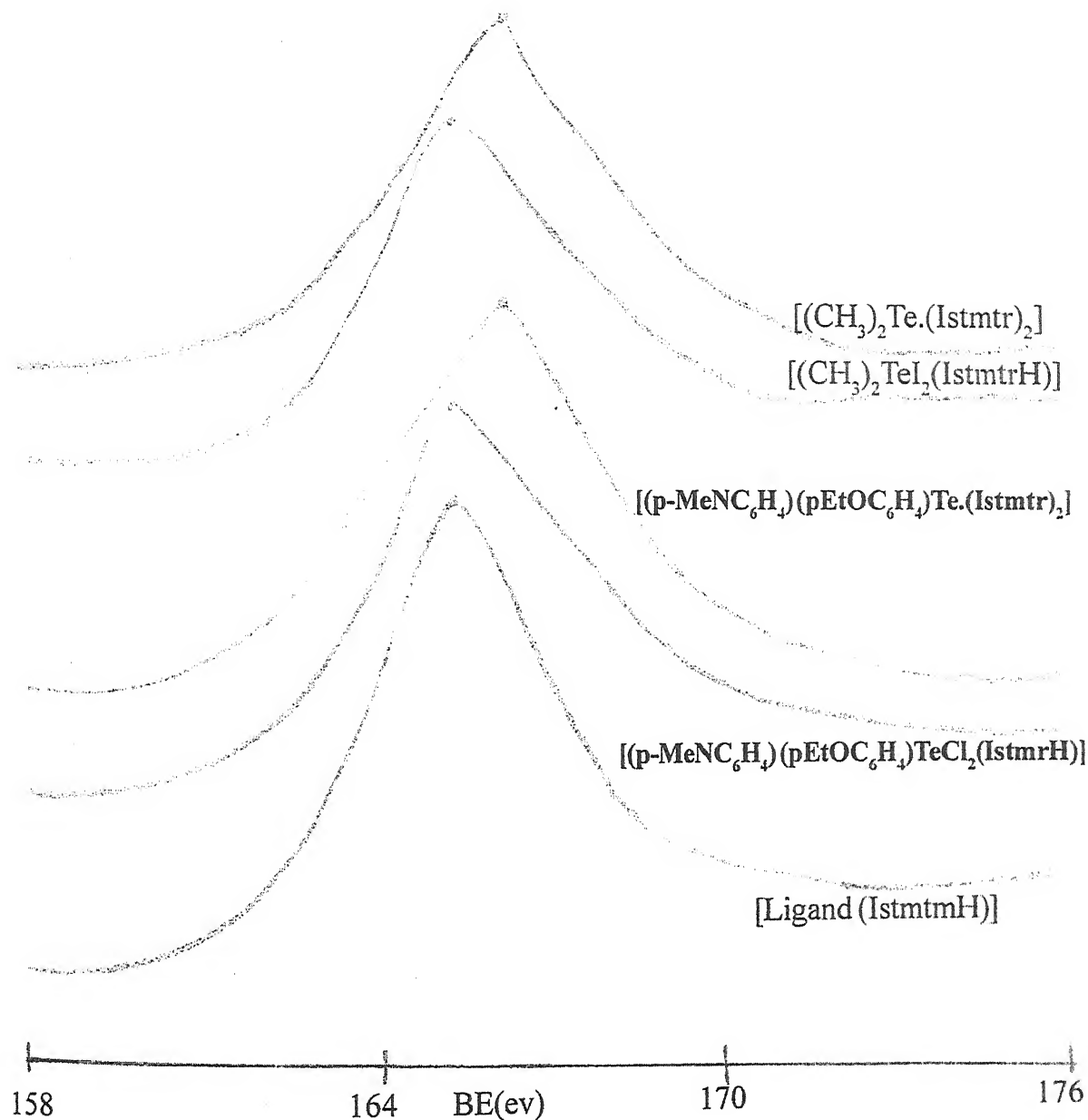and [R$_2$Te.(Istmtr)$_2$] complexes

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2. Y.D. Kulkarni and S. Srivastava : Indian J.Chem., 24A, 710(1985)
3. S.Srivastava : Applied spectro Sc. Rev., 22, 401(1986)

Chapter - V

"COMPLEXES OF R_2TeX_2 WITH α –PHENYL - SALICYLALDIMINO METHYL – β - NAPTHOL"

"COMPLEXES OF R₂TeX₂ WITH α – PHENYL - SALICYLALDIMINO-METHYL – β-NAPTHOL"

The Schiff base, α-phenylsalicylaldiminomethyl-β-napthol (i.e. pSnH$_2$) is potential tridentate (O,N,O) donor ligand and is expected to behave as monoanionic or dianionic coordinating molecular by deprotonation of one phenolic OH or both phenolic OH respectively.
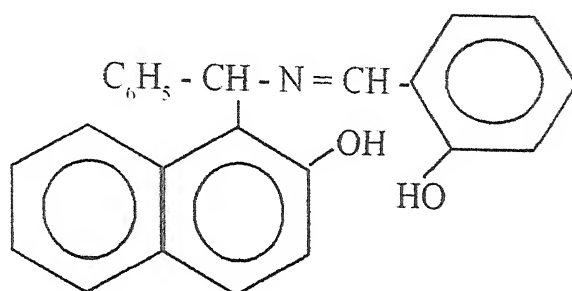
α - phenylsalicylaldiminomethyl - β - napthol (i.e. psnH$_2$)

Although many molecular adducts of R₂TeX₂ with various Schiff base ligands have been synthesized and characterized by various spectroscopy to establish their bonding, the interaction of R₂TeX₂ with ONO donor Schiff base ligands are scare [1]. This chapters deal with the interaction of R₂TeX₂ with α-phenylsalicylaldimino methyl-β-napthol (i.e. pSnH$_2$) and establish geometry of the products.

Preparation of [R₂Te(psn)]

The R₂TeX₂ (1mmol) i.e. (C₆H₅CH₂)TeI₂; (C₆H₄)₂TeCl₂; (p-MeOC₆H₄)TeCl₂; (p-Me₂N.CH₄)C₆H₅TeCl₂; (p-Me₂N.C₆H₄) (p-EtOC₆H₄)TeCl₂]; and (CH₃)₂TeI₂ was dissolved in 50 ml dry methanol and α-

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phenyl Salicylaldimino methyl-β-napthol i.e. (*p*SnH$_2$) (1mmol) was mixed in above solution drop by drop wise and mixture was refluxed for 3-4 hrs. The Resulting solid product was filtered washed with pet-ether and air-dried.

Preparation of [R$_2$Te.(psnH)$_2$]

The R$_2$TeX$_2$ (1mmol) i.e. (C$_6$H$_5$CH$_2$)TeI$_2$; (C$_6$H$_4$)$_2$TeCl$_2$; (*p*-MeOC$_6$H$_4$)$_2$TeCl$_2$; (*p*-Me$_2$N.CH$_4$)C$_6$H$_5$TeCl$_2$; (*p*-Me$_2$N.C$_6$H$_4$) (*p*-EtOC$_6$H$_4$)TeCl$_2$]; and (CH$_3$)$_2$TeI$_2$ was dissolved in 50 ml dry methanol and α-phenyl Salicylaldimino methyl-β-napthol i.e. (*p*SnH$_2$) (2mmol) was mixed in above solution. The mixture was refluxed for 3-4 hrs. and the resulting solid product was obtained,filtered . It washed with pet-ether and air-dried.

RESULT AND DISCUSSIONS

The all prepared complexes [R$_2$Te(*p*Sn)] and [R$_2$Te.(*p*SnH)$_2$] were found to be air stable. The molar conductance values of all the complexes in acetone were observed 20-30 ohm^{-1} cm^2 mol^{-1} indicating they are non electrolyte in nature[2].

The free ligand displays a strong broad band at 3270-3220 cm^{-1} attributed from νOH of phenolic group of ligand. The νOH of ligand disappeared in these [R$_2$Te(psn)] complexes suggesting deprotonation of both penolic proton in the complexes. But in case of [R$_2$Te.(*p*SnH)$_2$] . Its presence was observed.

The strong band at 1620 cm^{-1} in free ligand is attributed to $\nu_{C=N}$ which shifts to lower frequency in almost all the complexes suggesting coordination of aldimino ν(C=N) nitrogen to metal ion. The far IR for ν_{Te-N}, ν_{Te-C} were

appeared at 420-410 and 560-540 cm⁻¹ in all these prepared complexes³, while V_{Te-Cl} was found absent which normally appear at 270 - 300 cm⁻¹.
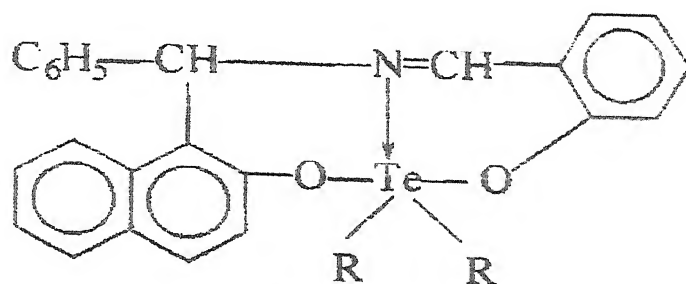
Structure of [R₂Te. (psn)]
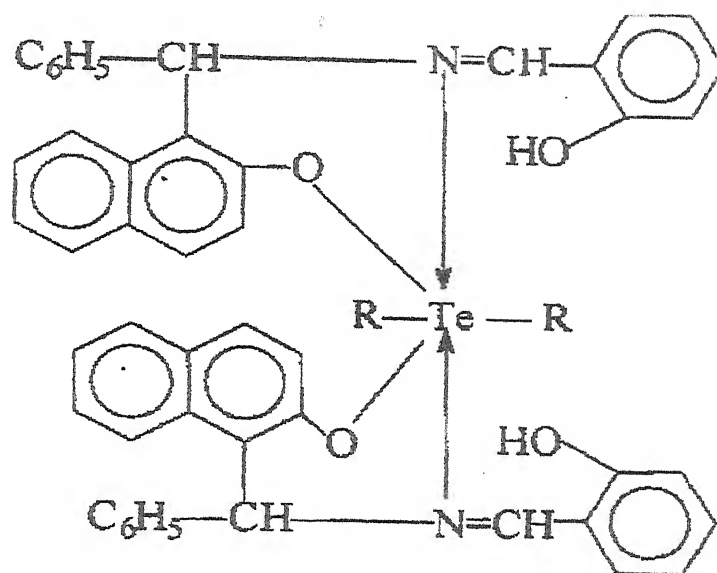
Structure of [R₂Te.(psnH)₂]

XPS data of Te3d$_{3/2, 5/2}$, N1s and O1s [R₂Te(psn)] and [R₂Te(psnH)₂] complexes are listed in table 2. It was observed that the binding energy of Te 3d$_{3/2, 5/2}$ in the starting material was higher than their prepared molecular adducts. These observations concluded that electron density on tellurium metal ion has been increased by coordination of Schiff base ligands with tellurium metal ion. [4](Fig 1and 2).

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It was noticed that N1s binding of C=N group were higher in all these [R_2Te.(pSn)] and [R_2Te($p$snH)$_2$] complexes than ligands; suggesting involvement of nitrogen atom of (C=Ngroup) in the complexation (Fig. 4 and 5). Furthermore, it was noticed 01s binding energy were more in [R_2Te($p$sn)] and [R_2Te($p$snH)$_2$] complexes, than ligands suggesting the involvement of oxygen atom in the complexes[4]. In case of [R_2Te($p$snH)$_2$] complexes 01s photoelectron peak have shown two peaks with same intensity , one wth same position as in ligand and other higher than ligand suggesting only two oxygen atoms are involved in coordination, remaining two oxygen atoms are uncoordinated4.(Fig. 5 and 6).

The X2p photoelectron spectra (x = Cl or I) were observed absent in [R_2Te(PsnH)$_2$] complexes and [R_2Te(psn)$_2$] complexes.

On the basis of elemental analysis, molar conductivity, IR and XPS data, it is possible to conclude that prepared molecular adducts [R_2Te(psn)] have octahedral structure, while [R_2Te($p$snH)$_2$] molecular adducts are pseudo octahedral in geometry as shown in fig. 7(a) and fig. 7(b).
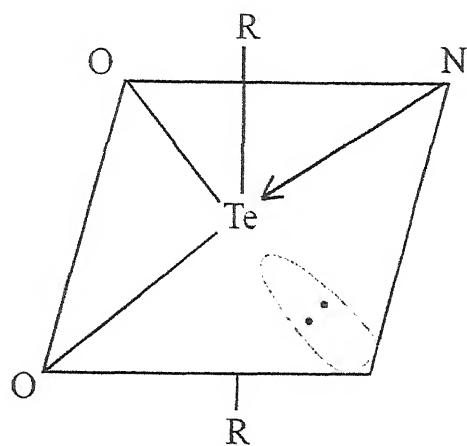
Geometry of [R_2Te ($p$sn)]   Structure of |R_2Te($p$snH)$_2$|
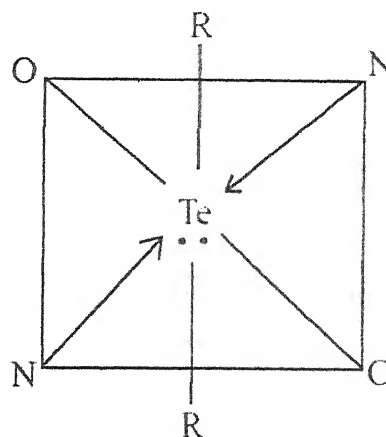
(a)   (b)

Fig. 7 : Geometry of |R_2Te($p$sn)| and |R_2Te($p$snH)$_2$| complexes

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Table 1: Elemental and molar conductivity of [R₂Te(pSn)] and [R₂Te(pSnH)₂] complexes

S.No.	Compound	Found (Calc.) (%)				Molar Conductivity (ohm^{-1} cm^2 mol^{-1})
		Te	C	H	N	
1.	[(C₆H₅CH₂)₂Te (pSn)]	19.0 (19.3)	69.1 (69.0)	4.5 (4.7)	2.0 (2.1)	10
2.	[(C₆H₄)₂Te.(pSn)]	20.2 (20.0)	68.2 (68.7)	3.4 (3.9)	2.0 (2.2)	15
3.	[(p-MeOC₆H₄)₂ Te(pSn)]	19.2 (19.3)	69.2 (69.0)	4.5 (4.6)	2.0 (2.1)	22
4.	[(p-Me₂NC₆H₄) C₆H₅Te.(psn)]	16.2 (16.0)	69.2 (69.4)	5.2 (5.3)	5.2 (5.3)	24
5.	[(p-Me₂NC₆H₄) (p-MeOC₆H₄)Te.(pSn)]	18.2 (18.0)	66.2 (66.3)	4.6 (4.8)	3.8 (3.9)	28
6.	[(p-Me₂NC₆H₄) (p-EtOC₆H₄)Te.(pSn)]	17.2 (17.3)	65.0 (65.1)	5.0 (5.0)	3.6 (3.8)	18
7.	[(CH₃)₂Te.(pSn)]	24.6 (24.8)	2.6 (2.7)	4.2 (4.5)	6.0 (6.2)	16
8.	[(C₆H₅CH₂)₂Te.(pSnH)₂]	12.4 (12.6)	73.4 (73.5)	4.6 (4.7)	2.6 (2.7)	12
9.	[(C₆H₄)₂Te.(pSnH)₂]	12.8 (12.9)	73.2 (73.3)	4.2 (4.0)	2.8 (2.9)	14
10.	[(p-MeOC₆H₄)₂Te(pSnH)₂]	12.0 (12.2)	71.0 (71.2)	4.5 (4.6)	2.6 (2.7)	16
11.	[(p-Me₂NC₆H₄) C₆H₅Te (psnH)₂]	12.2 (12.4)	72.4 (72.5)	4.6 (4.8)	4.2 (4.0)	12
12.	[(p-Me₂NC₆H₄) (p-MeOC₆H₄)Te.(pSnH)₂]	12.2 (12.4)	71.3 (71.6)	4.6 (4.7)	4.0 (4.0)	18
13.	[(p-Me₂NC₆H₄) (p-EtOC₆H₄)Te.(pSn)]	12.2 (12.0)	72.6 (72.8)	5.2 (5.0)	3.4 (3.9)	20
14.	[(CH₃)₂Te.(pSnH)₂]	14.6 (14.8)	69.6 (69.7)	4.2 (4.6)	3.0 (3.2)	22

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Table 2:- Te3d$_{3/2,5/2}$ N1s and 01s binding energies (ev) in (IstmtrH),[R$_2$TeX$_2$.(pSn)] and [R$_2$Te.(pSnH)$_2$] complexes

S.No.	compounds	Metal Te3d$_{3/2}$	Ion Te3d$_{5/2}$	01s	N1s
1.	Ligand(psnH)$_2$	-	-	532.6	399.0
2.	(C$_6$H$_5$CH$_2$)$_2$TeI$_2$	585.8	575.4	-	-
3.	[(C$_6$H$_5$CH$_2$)$_2$Te(pSn)]	584.2	574.0	534.4	400.8
4.	[(C$_6$H$_5$CH$_2$)$_2$Te(pSnH)$_2$]	584.2	574.0	532.6-534.4	400.8
5.	(C$_6$H$_4$)$_2$TeCl$_2$	585.6	575.2	-	-
6.	[(C$_6$H$_4$)$_2$Te(pSn)]	584.2	574.0	534.4	400.8
7.	[(C$_6$H$_4$)$_2$Te(pSnH)$_2$]	584.2	574.0	532.6-534.4	400.8
8.	[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$]	585.8	575.4	-	-
9.	[(p-MeOC$_6$H$_4$)$_2$Te(psn)]	584.2	574.0	534.4	400.8
10.	[(p-MeOC$_6$H$_4$)$_2$Te(psnH)$_2$]	584.2	574.0	532.6-534.4	400.8
11.	[(p-Me$_2$NC$_6$H$_4$) C$_6$H$_5$TeCl$_2$]	585.6	575.6		-
12.	[(p-Me$_2$NC$_6$H$_4$C$_6$H$_5$Te(psn)]	584.0	574.2	534.4	400.8
13.	[(p-Me$_2$NC$_6$H$_4$)$_2$ C$_6$H$_5$Te(psnH)$_2$]	584.0	574.2	532.6-534.4	400.8
14.	[(p-Me$_2$NC$_6$H$_4$) (p-MeOC$_6$H$_4$)TeCl$_2$]	585.8	575.4	-	-
15.	[(p-Me$_2$NC$_6$H$_4$) (p-MeOC$_6$H$_4$)Te.(psn)]	584.0	574.2	534.6	400.8
16.	[(p-Me$_2$NC$_6$H$_4$) (p-MeOC$_6$H$_4$)Te.(psnH)$_2$]	584.0	574.2	532.6-534.6	400.8
17.	[(p-Me$_2$NC$_6$H$_4$) (p-EtOC$_6$H$_4$)TeCl$_2$]	585.4	575.6	-	-
18.	[(p-Me$_2$NC$_6$H$_4$) (p-EtOC$_6$H$_4$)Te (psn)]	584.0	574.2	534.6	400.8
19.	[p-Me$_2$NC$_6$H$_4$ (p-EtOC$_6$H$_4$)Te(psnH)$_2$]	584.0	574.2	532.6-534.6	400.8
20.	[(CH$_3$)$_2$ TeI$_2$]	585.6	575.8	-	-
21.	[(CH$_3$)$_2$Te(psn)]	584.0	574.2	534.6	400.8
22.	[(CH$_3$)$_2$Te(psnH)$_2$]	584.0	574.2	532.6-534.6	400.8

Te3d$_{3/2}$ photoelectron peak.

[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te.(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te(psn)]

[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)TeCl$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te.(psnH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te(psn)]

[(p-MeOC$_6$H$_4$)$_2$TeCl$_2$]

[(C$_6$H$_4$)$_2$Te.(psnH)$_2$]

[(C$_6$H$_4$)$_2$Te(psn)]

[(C$_6$H$_4$)$_2$TeCl$_2$]

[(C$_6$H$_5$CH$_2$)$_2$Te.(psnH)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$Te(psn)]

[(C$_6$H$_5$CH$_2$)$_2$TeI$_2$)]

586   582 BE(ev)   588   594
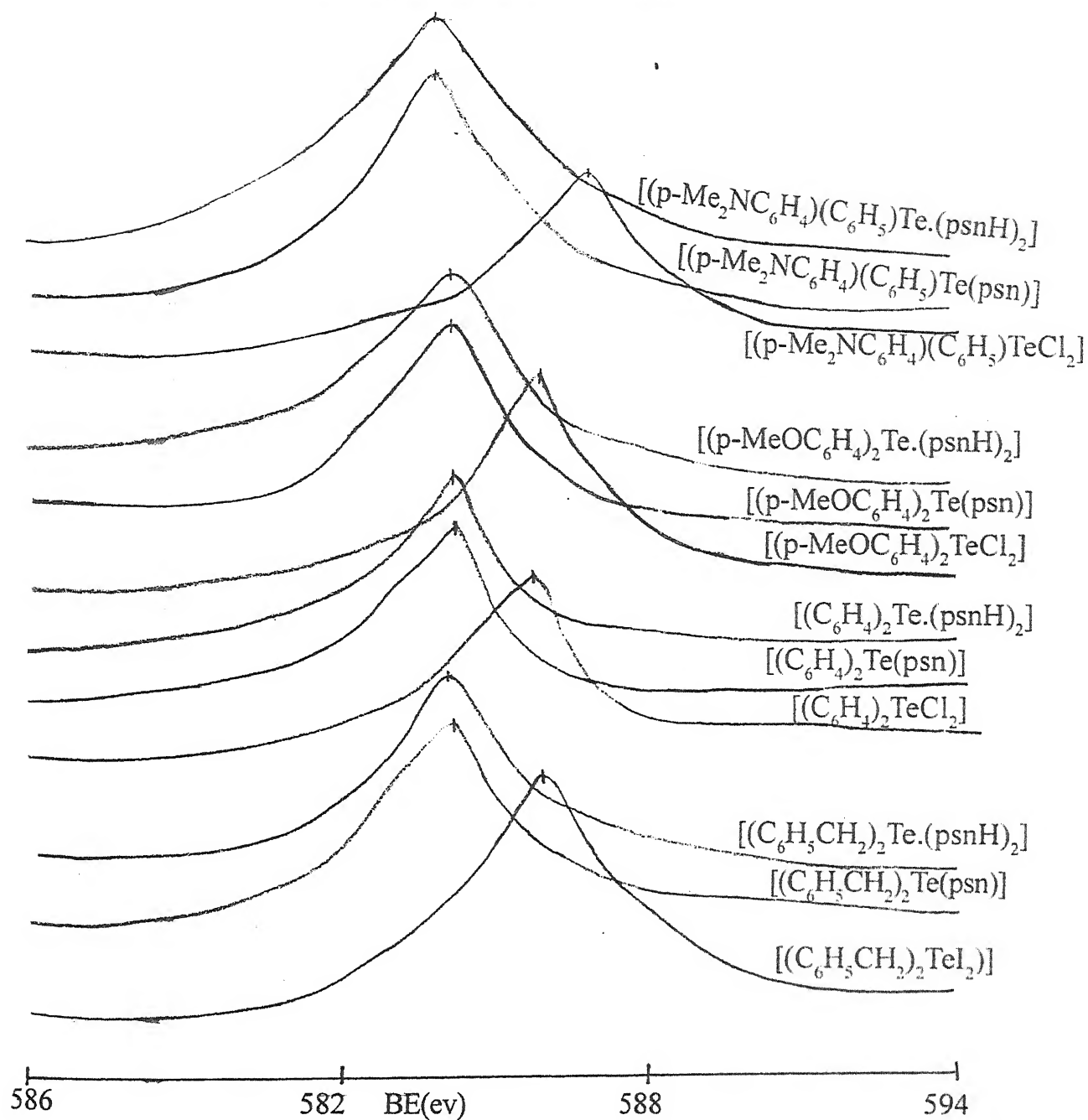
Fig 1 : Te 3d$_{3/2}$ binding energies (ev) in [R$_2$TeX$_2$]; [R$_2$Te(psn)]
and [R$_2$Te.(psnH)$_2$] complexes

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Te3d$_{3/2}$ photoelectron peak.

[(CH$_3$)$_2$Te.(psnH)$_2$]

[(CH$_3$)$_2$Te(psn)]

[(CH$_3$)$_2$TeI$_2$]

[(p-Me$_2$NC$_6$H$_4$)$_2$(p-EtOC$_6$H$_4$)Te.(psnH)$_2$]

[(p-MeNC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(psn)]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)TeCl$_2$]

[(p-Me$_2$NC$_6$H$_4$)(pMeOC$_6$H$_4$)Te.(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(pMeOC$_6$H$_4$)Te(psn)]

[(p-Me$_2$NC$_6$H$_4$)(pMeOC$_6$H$_4$)TeCl$_2$]

576   582   BE(ev)   588   594
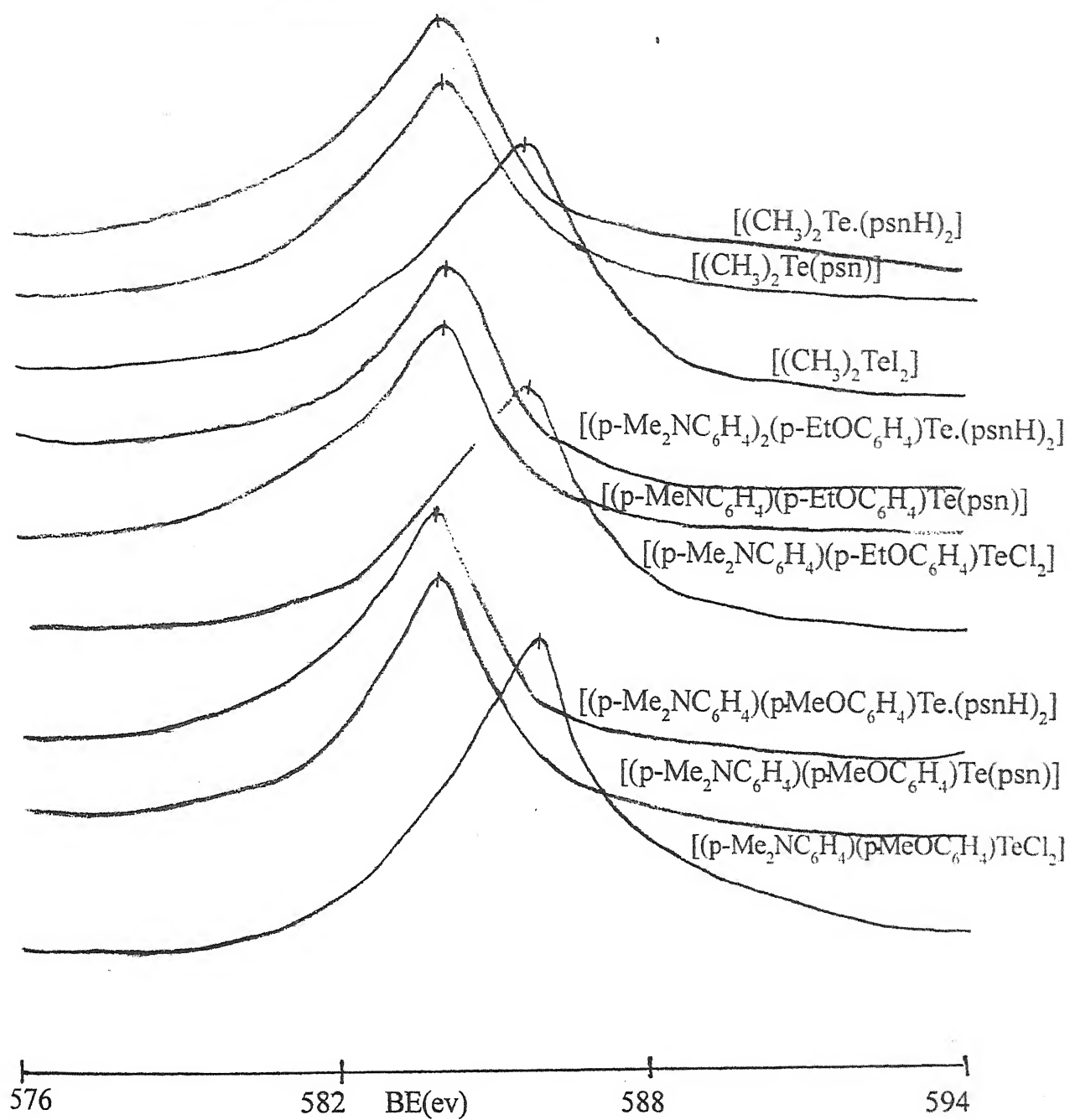
Fig 2 : Te 3d$_{3/2}$ binding energies (ev) in R$_2$TeX$_2$; [R$_2$Te(psn)$_2$] and [R$_2$Te.(psnH)$_2$] complexes

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N1s photoelectron peak

[(p-Me$_2$NC$_6$H$_4$)(C$_6$H$_5$)Te.(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(psn)]

[Ligand (psnH$_2$)]

[(p-MeOC$_6$H$_4$)$_2$Te.(psnH)$_2$]

[(p-MeOC$_6$H$_4$)$_2$Te(psn)]

[Ligand (psnH$_2$)]

[(C$_6$H$_4$)$_2$Te.(psnH)$_2$]

[(C$_6$H$_4$)$_2$Te(psn)]

[Ligand (psnH$_2$)]

[(C$_6$H$_5$CH$_2$)$_2$Te.(psnH)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$Te.(psn)]

[Ligand = psnH$_2$]

390   396   BE(ev)   402   408

Fig 3 : N1s binding energies (ev) in Ligand, (psnH$_2$), [R$_2$Te(psn)]
and [R$_2$Te.(psnH)$_2$] complexes

N1s photoelectron peak

$[(CH_3)_2Te.(psnH)_2]$

$[(CH_3)_2Te(psn)]$

Ligand = $psnH_2$

$[(p-Me_2NC_6H_4)(p-EtOC_6H_4)Te.(psnH)_2]$

$[(p-Me_2NC_6H_4)(p-EtOC_6H_4)Te(psn)]$

Ligand $(psnH_2)$

$[(p-Me_2NC_6H_4)(p-MeOC_6H_4)Te.(psnH)_2]$

$[(p-Me_2NC_6H_4)(p-MeOC_6H_4)(psn)]$
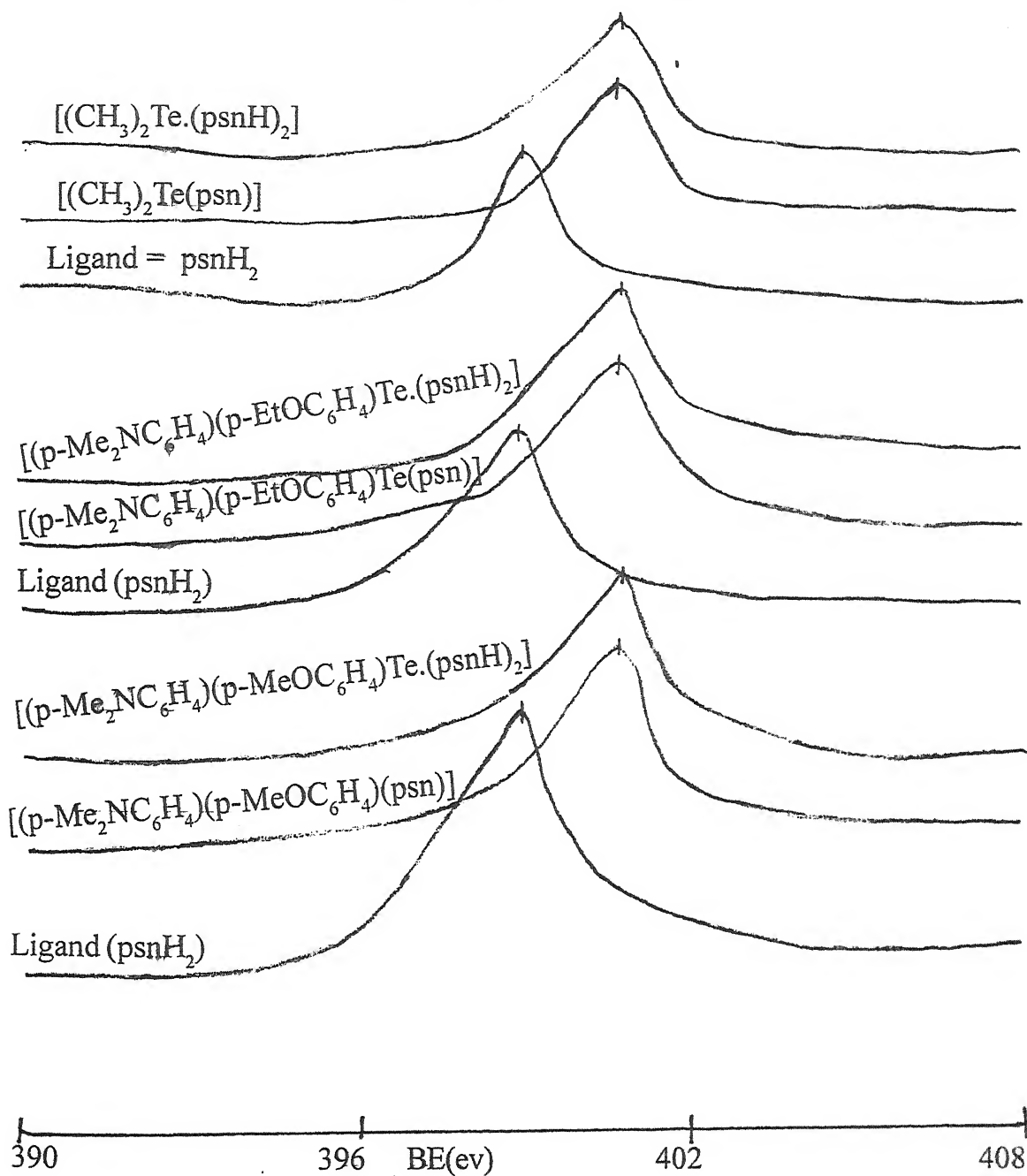
Ligand $(psnH_2)$

390   396   BE(ev)   402   408

Fig 4 : N1s binding energies (ev) in Ligand, $(psnH_2)$, [R2Te(psn)]
and $[R_2Te.(psnH)_2]$ complexes

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O1s photoelectron peak

[(CH$_3$)$_2$Te.(psnH)$_2$]
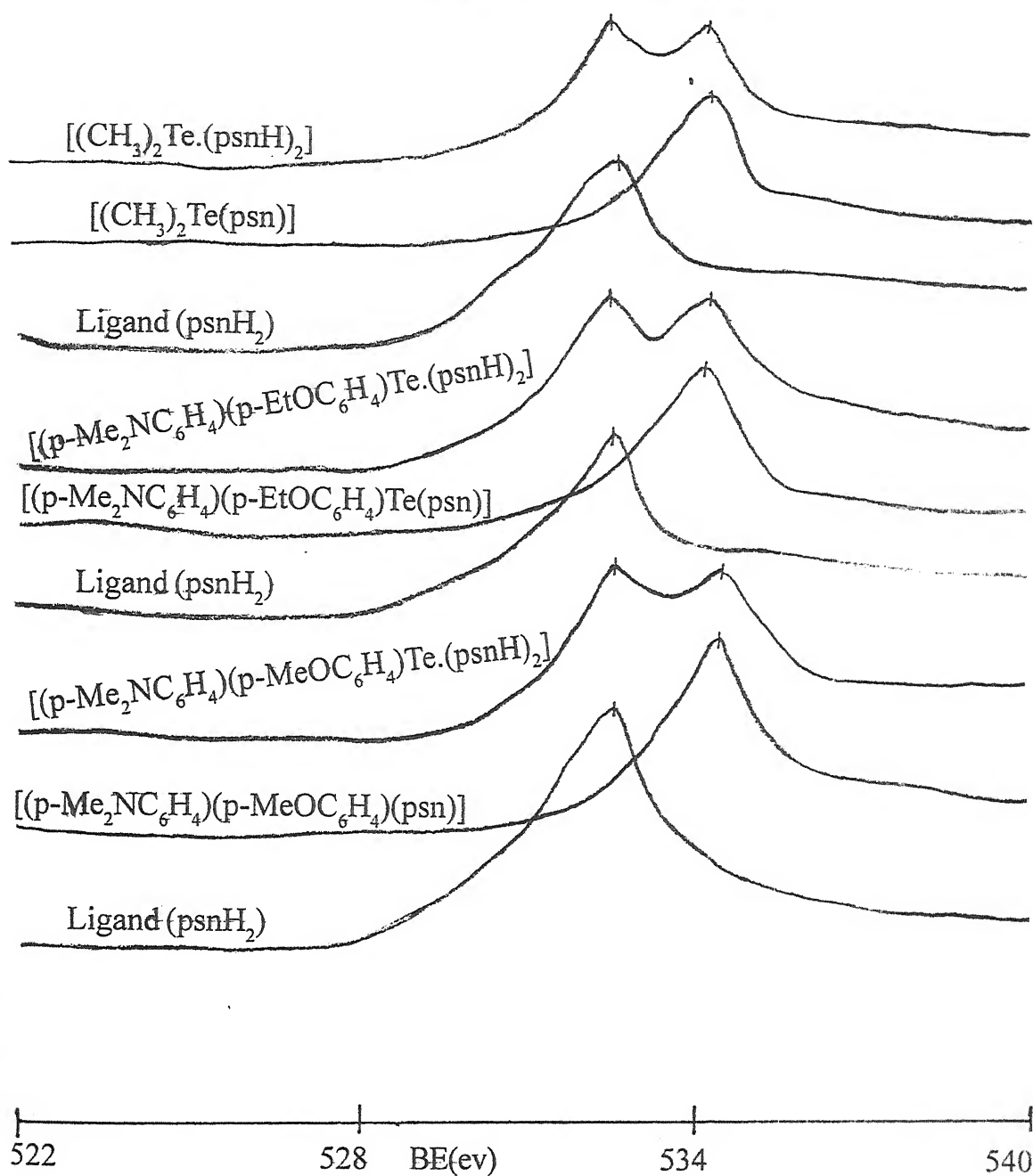
[(CH$_3$)$_2$Te(psn)]

Ligand (psnH$_2$)

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te.(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-EtOC$_6$H$_4$)Te(psn)]

Ligand (psnH$_2$)

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)Te.(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)(p-MeOC$_6$H$_4$)(psn)]

Ligand (psnH$_2$)

522 528 BE(ev) 534 540

Fig 5 : O1s binding energies (ev) in Ligand, [R$_2$Te(psn)]
and [R$_2$Te.(psnH)$_2$] complexes

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O1s photoelectron peak

[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(psnH)$_2$]

[(p-Me$_2$NC$_6$H$_4$)C$_6$H$_5$Te(psn)]

[Ligand (psnH$_2$)]

[(p-MeOC$_6$H$_5$)$_2$Te(psnH)$_2$]

[(p-MeNC$_6$H$_5$)$_2$Te(psn)]

[Ligand (psnH$_2$)]

[(C$_6$H$_4$)$_2$Te(psnH)$_2$]

[(C$_6$H$_4$)$_2$Te(psn)]

[Ligand (psnH$_2$)]

[(C$_6$H$_5$)$_2$Te.(psnH)$_2$]

[(C$_6$H$_5$CH$_2$)$_2$Te.(psn)]

[Ligand (psnH$_2$)]

522　　　　528　　BE(ev)　　534　　　　540

Fig 6 : O1s binding energies (ev) in Ligand, [R$_2$Te(psn)]
and [R$_2$Te.(psnH)$_2$] complexes

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CHAPTER - VI

SUMMARY

The elements of group VI A have a general electronic configuration [x] $npx^2npx^1npz^1$ (where x = inert gas core and n = 2 to 6 from oxygen to polonium) and tend to attain an inert gas configuration by gaining or sharing two electrons. Only few compounds are known which are more than 50% ionic for Te electropositive elements. The known formal oxidation state for tellurium are II and IV.

In chapter III, tellurium is in IV oxidation state in R_2TeX_2 which form with $SamtrH_2$ or $5Me - SamtrH_2$ or $5Ph-SamtrH_2$ ligand $[R_2Te(Satrm)]$ complexes and $[R_2Te.(SatrmH)_2]$ complexes and their established geometry are as given below:
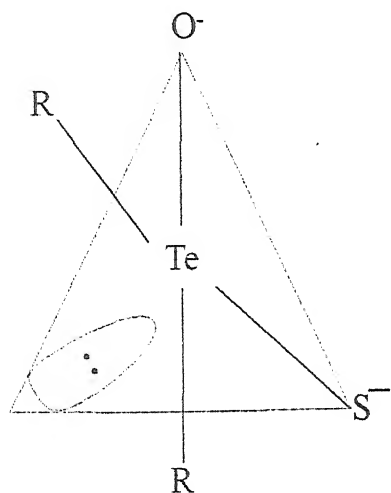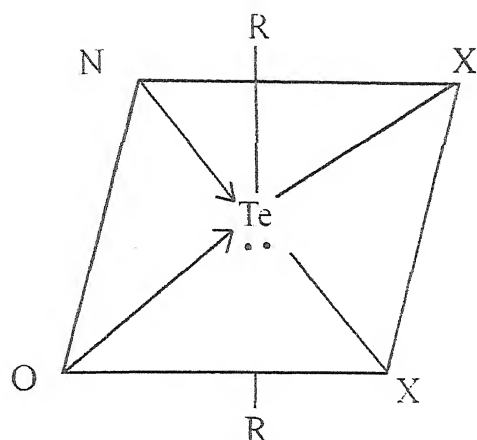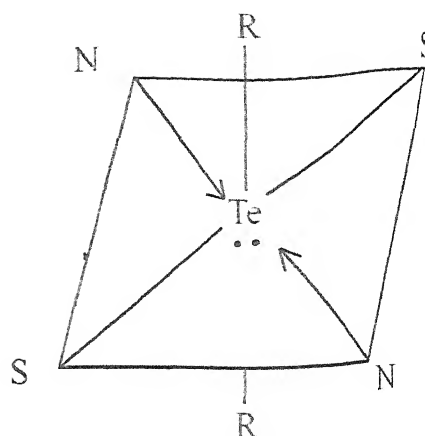

[R_2Te(samtr)]
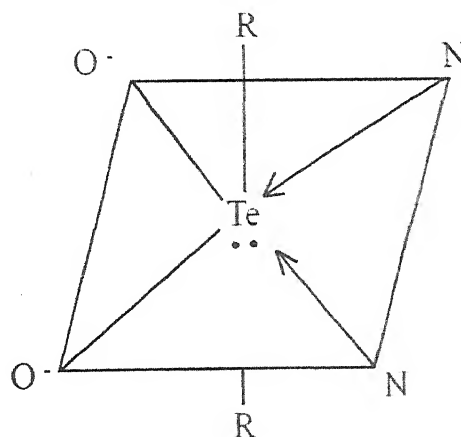
[R_2Te $(SamtrH)_2$]
(pseudooctahedral)

In chapter IV, the acceptor property of R_2TeX_2 with 3 – mercapto – 4 β – isatinylimino – 1, 2, 4 triazole in 1:1 and 1:2 molar ratio have been studied. it was established $[R_2Te(Istmtr)_2]$ and $[R_2TeX_2(IstmtrH)]$ molecular adducts with all octahedral i.e. (sp^3d^3) geometry as given below.

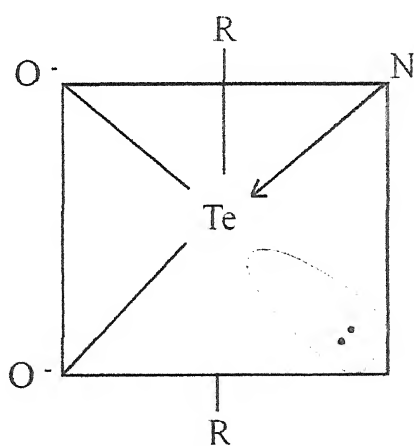(180)

Geometry of [R$_2$Te (IsamtrH)$_2$]

Geometry of [R$_2$Te (Istmtr)$_2$]
complexes

In chapter V, the acceptor property of R$_2$TeX$_2$ with α – phenyl salicylaldimino methyl – β – naphthol in 1:1 and 1:2 molar ratio have been studied and it was established [R$_2$Te(psn)] and [R$_2$Te(psnH)$_2$] molecular adducts with all octahedral and pseudooctahedral geometry respectively.

Geometry of [R$_2$Te(psn)]
(octahedral)
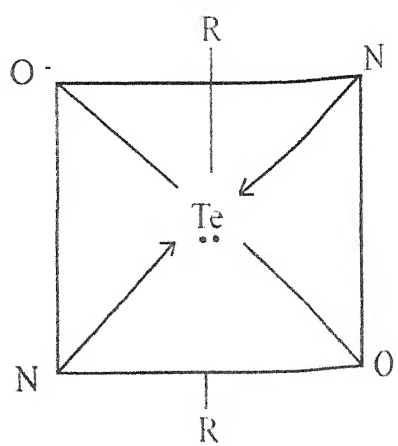
Geometry of [R$_2$Te(psnH)$_2$]
(pseudooctahedral)

These prepared molecular adducts of R$_2$TeX$_2$ may be useful as antibacterial action[1], as medicine[2], as polymer[3-4], as Therapeutic agents[4-5], as oxi-

dants[6-7], antiknocking agents[6-7], in photochemical preparation[6-7], photoconductors insecticides[6-7], lubricating oil additives[6-7], pharmacological agents[6-7], corrosion inhibitors[6-7] etc.

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